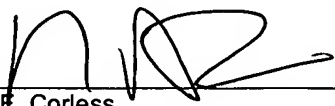
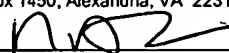




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JW

TRANSMITTAL OF APPEAL BRIEF			Docket No. 55567(72011)
In re Application of: Craig A. Willkens			
Application No. 10/090,468-Conf. #5103	Filing Date March 4, 2002	Examiner D. L. Robinson	Group Art Unit 3742
Invention: CERAMIC IGNITERS			
<p style="text-align: center;"><u>TO THE COMMISSIONER OF PATENTS:</u></p> <p>Transmitted herewith is the Appeal Brief in this application, with respect to the Examiner's Answer date August 14, 2006 and Notification of Non-Compliant Appeal Brief (37 CFR 41.37) dated September 28, 2006</p> <p>The fee for filing this Appeal Brief is <u>Already submitted</u>.</p> <p><input checked="" type="checkbox"/> Large Entity <input type="checkbox"/> Small Entity</p> <p><input type="checkbox"/> A petition for extension of time is also enclosed.</p> <p>The fee for the extension of time is _____.</p> <p><input type="checkbox"/> A check in the amount of _____ is enclosed.</p> <p><input checked="" type="checkbox"/> Charge the amount of the fee to Deposit Account No. <u>04-1105</u>. This sheet is submitted in duplicate.</p> <p><input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.</p> <p><input checked="" type="checkbox"/> The Director is hereby authorized to charge any additional fees that may be required or credit any overpayment to Deposit Account No. <u>04-1105</u>. This sheet is submitted in duplicate.</p> <div style="display: flex; justify-content: space-between; align-items: flex-end;"><div style="width: 60%;"> _____ Peter F. Corless Attorney Reg. No. : 33,860 EDWARDS ANGELL PALMER & DODGE LLP P.O. Box 55874 Boston, Massachusetts 02205 (617) 439-4444</div><div style="width: 35%; text-align: right;">Dated: <u>October 16, 2006</u></div></div>			
<div style="border: 1px solid black; padding: 5px;"><p>I hereby certify that this paper (along with any paper referred to as being attached or enclosed) is being deposited with the U.S. Postal Service as Express Mail, Label No. EV894053050US, on the date shown below in an envelope addressed to: MS Appeal Brief - Patents, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.</p><div style="display: flex; justify-content: space-between;"><div>Dated: October 16, 2006</div><div>Signature:  (Peter F. Corless)</div></div></div>			



Docket No. 55567
Express Mail Label No EV894053050US

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES**

APPLICANT: C. Willkens
SERIAL NO.: 10/090,468 GROUP: 3742
FILED: March 4, 2002 EXAMINER: J. Jeffrey
FOR: CERAMIC IGNITERS

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P. O. Box 1450
Alexandria, VA 22313-1450

**RESPONSE TO EXAMINER'S ANSWER AND NOTIFICATION
OF NON-COMPLIANT APPEAL BRIEF**

Applicant received 1) an Examiner's Answer dated August 14, 2006 and 2) a Notification of Non-Compliant Appeal Brief dated September 28, 2006.

In response, Applicants file herewith an amended Appeal Brief.

In specific response to the Examiner's Answer, it is stated in the Examiner's Answer "Please amend the Appeal Brief and discuss claim 1 and the prior art. The Appeal Brief filed herewith has been amended in such manner. Thus, claim 1 is discussed in the "Summary of Claimed Subject Matter" section of the Appeal Brief submitted herewith. Claim 1 also has been specifically discussed in the "Argument" section of the Appeal Brief submitted herewith.


C. Willkens
U.S.S.N. 10/090,468
Page 2

In specific response to the Notification of Non-Compliant Appeal Brief, it is stated in that Notice "Heading X (Related Proceedings Appendix) is missing from the appeal brief." That Related Proceedings Appendix is missing from the Appeal Brief because no items exist to include in that appendix. This is acknowledged in the Examiner's Answer (the Answer states "The examiner is not aware of any related appeals, interference, or judicial proceedings which will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.").

Nevertheless, the Appeal Brief submitted herewith includes a Related Proceedings Appendix, although no items are included in that Appendix.

Respectfully submitted,

Date: Oct. 14, 2000

By: 
Peter F. Corless (Reg. No. 33,860)
EDWARDS ANGELL PALMER & DODGE, LLP
P. O. Box 55874
Boston, MA 02205
Tel. (617) 439-4444
Fax (617) 439-4170 / 7748
Customer No.: 21874



Docket No. 55567
Express Mail Label No EV894053050US

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES**

APPLICANT: C. Willkens
SERIAL NO.: 10/090,468 GROUP: 3742
FILED: March 4, 2002 EXAMINER: J. Jeffrey
FOR: CERAMIC IGNITERS

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APPEAL BRIEF

Applicant respectfully appeals the decision of the Examiner, dated June 27, 2005, finally rejecting claims 1-11, 14-19 and 21-33.



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Claims Appendix A: Claims 1-11, 14-19 and 21-33 on appeal

Evidence Appendix B: Rule 132 Declaration of Dr. Taehwan Yu filed February 26, 2004

Patents Appendix C: U.S. Patent 5705261 to Axelson; U.S. Patent 5786565 to Willkens;
U.S. Patent 5045237 to Washburn

Related Proceedings Appendix D: (no materials)

I. REAL PARTY IN INTEREST

The real party in interest is Saint-Gobain Ceramics & Plastics, Inc. of Worcester, Massachusetts. An assignment from the inventors to Saint-Gobain Ceramics & Plastics, Inc. was recorded on July 17, 2002 at Reel/ Frame 013009/0967.

II. RELATED APPEALS AND INTERFERENCES

There are no related appeals or interferences known to Appellant or Appellant's representatives that will directly affect or be directly affected by or have a bearing on the Board's decision in the pending Appeal.

III. STATUS OF THE CLAIMS

Claims 1-33 have been presented in this application.

Claims 12, 13, and 20 have been cancelled.

Claims 1-11, 14-19 and 21-33 have been finally rejected and presently are on appeal (see the attached Appendix A).

Claims 1 and 26 are the two independent claims on appeal.

IV. STATUS OF THE AMENDMENTS (AFTER FINAL REJECTION)

No amendments after final rejection have been presented.

V. SUMMARY OF CLAIMED SUBJECT MATTER

Appellant's claimed invention is directed to ceramic igniter devices that have a first conductive zone of relatively low resistance, a power enhancement or "booster" zone of intermediate resistance, and a further hot or ignition zone of relatively higher resistance. See application at page 3, lines 17-20.

Appellant's independent claims 1 and 26

Appellant has two pending independent claims on appeal: claims 1 and 26. Those claims read as follows:

Claim 1. A sintered ceramic igniter element comprising a conductive zone, a power booster zone, and a hot zone,
the booster zone having a PTCR and a resistivity greater than the conductive zone and less than the hot zone,
the hot zone having a resistivity greater than the booster zone,
wherein the hot zone path length is 2 cm or less and the igniter has a time-to-temperature value of 3 seconds or less.

Claim 26. A sintered ceramic igniter element comprising a conductive zone, a power booster zone, and a hot zone,
the booster zone having a PTCR and a resistivity greater than the conductive zone and less than the hot zone,
the hot zone having a resistivity greater than the booster zone,
wherein

the hot zone path length is 2 cm or less;
the igniter has a time-to-temperature value of 3 seconds or less;
the room temperature resistance of the conductive zone is less than about 50 percent of the room temperature resistance of the booster zone; and
the room temperature resistance of the booster zone is less than about 70 percent of the room temperature resistance of the hot zone.

Figure 1 of the application

Figure 1 of the application is reproduced immediately below and depicts an exemplary ceramic igniter element as Appellant claims.

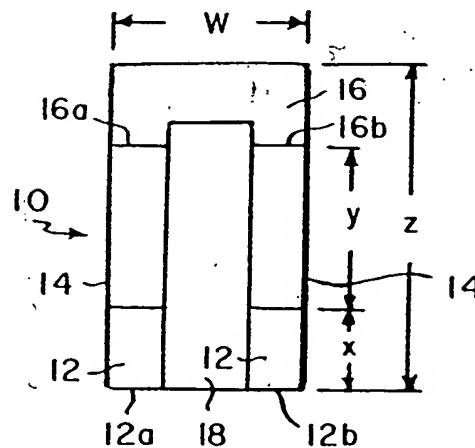


FIG. 1

In that Figure 1, igniter 10 includes conductive zones 12, adjoining power enhancement zones and a hot or ignition zone 16. In use, wire leads are connected to ends 12a and 12b of the conductive zone to supply power to the igniter, through booster zones 14 to hot zone 16. See application at page 8, lines 9-16.

Preferred igniters also may comprise an insulator region, such as centrally disposed heat sink 18 depicted in Figure 1. Among other things, such a heat sink region can prevent the igniter device from shorting (arcing). See application at page 8, lines 11-14. Such an insulator region is recited in Appellant's claims 23 and 24. See the attached Claims Appendix A.

Demonstrated rapid time-to-temperature performance

Appellant has surprisingly discovered that igniters of the invention can provide extremely fast time-to-ignition temperatures, include ignition times of 3 seconds or less, or even 2 seconds or less. See application at page 3, lines 8-31. This is demonstrated for instance by the results shown in Example 2 at page 15, lines 10-15 of the application, where ignition temperature was reached in less than 1 second.

Such results are clearly significant. Appellant's preferred rapid-ignition ceramic igniters can replace spark ignition systems where an extremely fast time-to-temperature is required. This is discussed for instance at page 3, line 28 through page 4, line 3 of the application as follows:

It has been surprisingly found that igniters of the invention can provide extremely high speeds, including time-to-temperature of less than two seconds, and even less than about one-and-one half seconds or about one second, at both nominal voltages and low-end line voltages (85 percent of a specified nominal voltage). See, for instance, Example 2 which follows. Thus, for the first time, ceramic igniters are provided that can replace spark ignition systems where an extremely fast time-to-temperature is required, e.g. for an ignition source for instantaneous water heating systems, cooktops, and the like.

All the pending claims call for a rapid time-to-temperature value. See independent claims 1 and 26 as well as dependent claims 16, 25, 27, and 33.

Hot zone path lengths of 2 cm or less

Appellant also has found that an excessive hot zone path length can compromise performance, particularly the time to reach ignition temperature. See the application at page 8, line 32 through page 9, line 2. In reference to Figure 1 of the application reproduced above, the hot zone path length is the minimum distance from points 16a to 16b. See the application at page 8, lines 31-32.

All the pending claims call for a hot zone path less of 2 cm or less.

Dr. Yu's Rule 132 Declaration of record

Of record is the Rule 132 Declaration of Dr. Taehwan Yu which details comparative data that demonstrate that ignition speed (i.e. time to targeted ignition temperature) decreases and temperature is reduced with increases in electrical path length of resistive hot zones of otherwise comparable igniter elements that have booster zone regions. A copy of Dr. Yu's Declaration is provided herewith at Evidence Appendix B. Dr. Yu's Declaration was filed on February 26, 2004.

VI. GROUND OF REJECTION TO BE REVIEWED ON APPEAL

A single issue in on appeal:

Whether claims 1-11, 14-19 and 21-23 are unpatentable under 35 U.S.C. §103 over Axelson (U.S. Patent 5705261) in view of Willkens (U.S. Patent 5786565).

VII. ARGUMENT

The following argument section addresses the single ground of rejection on appeal in this case.

1. **Brief summary of argument**

A single Section 103 rejection based on two documents is outstanding in this case. The rejection can not be sustained.

The proposed combination is not proper. No incentive would have existed to so carefully select and combine particular features of the two cited documents as has been proposed in the outstanding final rejection. The cited Willkens patent effectively teaches *against* the proposed combination.

The cited documents also do not disclose or otherwise suggest Appellant's claimed invention. In particular, the documents do not disclose hot zone lengths or ignition time-to-temperature values in an igniter having more than two zones of differing resistivity as Appellant claims. The cited documents also do not disclose booster zone operational temperatures, resistance differences of the booster zone relative to other igniter zones, and booster zone path length as Appellant claims.

Still further, the comparative results of record effectively rebut any *prima facie* case under Section 103 that may be contended to exist.

The rejected claims do *not* stand or fall together since each claim is considered separately patentable in its own right. Appellant believes that all of the claims under appeal are separately patentable including for reasons set forth below.

2. Examiner's position

It is acknowledged that neither of the cited documents alone renders obvious Appellant's claimed invention.

The position is nevertheless taken that it would have been obvious to carefully select and combine isolated feature of Axelson (U.S. Patent 5705261) in view of Willkens (U.S. Patent 5786565) and that careful combination would have rendered Appellant's claimed invention obvious.

In particular, it is acknowledged that the primary citation of Axelson does not disclose a hot zone path length of 2 cm or less as Appellant claims, but the position is taken that the cited Willkens patent reports a hot zone path length of 0.5 cm and that it would have been obvious to incorporate that hot zone into the Axelson system. See page 3 of the Final Office Action dated May 27, 2005.

It is further acknowledged that the primary citation of Axelson does not disclose a central insulator zone as Appellant claims, but the position is taken that the cited Willkens patent reports a central insulator zone and that it would have been obvious to incorporate that insulator zone into the Axelson device. See page 3 of the Final Office Action dated May 27, 2005.

Additional claimed aspects of Appellant's invention are acknowledged not to be disclosed in the cited documents – including ranges of conductor-to-booster zone resistivity, ranges of booster-to-hot zone resistivity, and booster zone length. However, in the final rejection, the position has been taken without any support from the prior art that such claimed features “are readily discoverable by routine experimentation by skilled artisans” and therefore not patentable.¹ See page 4 of the Final Office Action dated May 27, 2005.

¹ As discussed in the Argument section which follows, an unsupported allegation that claimed subject matters “are readily discoverable by routine experimentation by skilled artisans” is clearly improper and basis itself to reverse the final rejection in this case. See, for instance, Section 2143.03 of

At page 5-7 of the Final Office Action dated May 27, 2005, the comparative data of Dr. Yu's Rule 132 Declaration of record are characterized as being expected from the disclosure of the cited Willkens patent, even though that cited patent does not disclose igniters having a booster zone as Appellant claims.

3. Appellant's arguments

A. No incentive would have existed to combine the cited documents as proposed by the final rejection.

A booster zone of intermediate resistance is recited in all of Applicants' pending claims. See independent claims 1 and 22.

The entire rejection is based on an intermediate portion 14 reported in the of Axelson patent.

That intermediate portion 14 is disclosed as being *preferably omitted* for ease of manufacture. See the cited Axelson patent at col. 4, lines 30-32.

In the Examples of the Axelson patent, an intermediate zone is *not* described.

Additionally, the Axelson patent reports igniters that contain an interior void space, i.e. a hairpin or "slotted" igniter that does not contain an interposed heat sink zone.

The cited disclosure of the Willkens patent is to an igniter where the hot zone directly adjoins cold, conductive zones and a heat sink zone. The Willkens patent does not mention an intermediate zone as reported in the Axelson patent.

Indeed, at column 3, lines 30-35, the cited Willkens patent notes the importance of the heat sink zone for the described system having a short hot zone length as follows:

Without wishing to be tied to a theory, it is believed the added thermal mass of the heat sink significantly slows convective cooling of the hot zone, thereby allowing the hot zone to remain hot under convective cooling conditions despite its small size.

Thus, the cited Willkens patent effectively teaches *against* use of the reported short hot zone lengths in systems that do not include a heat sink.

Clearly, then, a skilled worker would *not* have had any particular incentive to select a single feature (hot zone length) of the cited igniter of the Willkens patent with a heat sink zone and insert that selected aspect into a distinct igniter that does not contain an interposed heat sink zone. This is particularly clear where the Willkens patent urges coupling an interposing heat sink region together with the described hot zone length.

B. The cited documents do not disclose or otherwise suggest Appellant's claimed invention.

As specifically acknowledged in the Final Office Action, the Axelson patent does not mention or otherwise suggest:

- (1) booster zone operational temperatures as recited in Appellant's claims 6-8;
- (2) resistance differences of the booster zone relative to other igniter zones as recited in Appellant's claims 9, 10, 11, 28 and 39; and
- (3) booster zone path lengths as recited in Appellant's claims 21-22.

Indeed, in the Final Office Action, it is acknowledged that such claimed aspects of Appellant's invention are disclosed nowhere in the cited art, but the position is taken that those claimed subject matters "are readily discoverable by routine experimentation by skilled artisans." This position is completely unsubstantiated.

Such a position can not be sustained and is clear basis for reversal of the final rejection in this case. In fact, reversal of the final rejection here is required under Section 2143.03 of the Manual of Patent Examining Procedure, which mandates: "To establish *prima facie* obviousness of a claimed invention, all claim limitations must be taught or suggested by the prior art."

The Axelson patent also does not mention lengths of a hot zone, or the a hot zone path length, or the significance thereof, as Appellant discloses and claims. As discussed above and demonstrated by the comparative test results set forth in Dr. Yu's Declaration, the claimed hot zone path length of the present igniters having booster zones can be very important in achieving desired performance results.

If anything, the primary citation of the Axelson patent indicates use of quite long hot zone path lengths. Thus, Example 1 of the Axelson document states (column 5, lines 43-48 of the Axelson patent):

A double-legged hairpin ("U-shaped") ceramic igniter as shown in FIG. 1 was prepared ... in accordance with the teachings of the Washburn patent. [i.e. U.S. Patent 5,045,237, see col. 4, lines 19-21 of Axelson].

The Washburn patent (i.e. U.S. 5,045,237, copy enclosed) discloses igniters having a hot zone path length well in excess of 2 cm. See, for instance, U.S. Patent 5,045,237 at col. 7, line 62 through col. 8, line 3 and Example I and II at cols. 9 through 12.

The cited Willkens patent does not remedy such shortcomings of the primary citation.

The cited Willkens patent does not report an igniter region that correspond to Appellant's booster zone. Therefore, Willkens does not disclose that the reported hot zone path lengths might

be suitably employed with an igniter having more than two zones of differing resistivity as Appellants claim.

C. Comparative data of record effectively rebuts any *prima facie* case under Section 103 that may be contended to exist.

Moreover, while Appellant fully believes that a *prima facie* case under 35 U.S.C. 103 is not presented by the cited combination of documents, it is also believed that the test data of record fully rebuts any *prima facie* case that may be contended to exist.

Thus, as discussed above, the comparative test results set forth in Dr. Yu's Rule 132 Declaration of record show that insufficient hot zone temperatures and time-to-temperature values can be provided where an igniter with a booster has a hot zone path length in excess of 2 cm. See, in particular, Figures 1 and 2 of the Declaration.

These results support patentability of all the pending claims.

D. Each of the claims on appeal is separately patentable.

The cited Axelson and Willkens patents also provide no suggestion of other aspects of Appellant's claimed invention.

a) Claim 2

For instance, claim 2 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the igniter of claim 1 wherein the resistance of the booster zone permits i) current flow to the igniter hot zone and ii) resistance heating of the booster region during use of the igniter. As discussed above, the Axelson document is completely silent regarding any operational effects of the described system.

b) Claim 3

Claim 3 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the igniter of claim 1 or 2 wherein the resistance of the booster zone increases during application of current through the igniter and heating of the booster zone. Axelson – the sole document relied on for a report of something analogous to Appellant’s claimed booster zone – is completely silent regarding any type of operational effects of an igniter having more than two zones of differing resistivities. Axelson does not exemplify an igniter having more than two zones of differing resistivities.

c) Claim 5 and 6

Claims 5 and 6 each is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the igniter of claim 1 wherein the three zones (conductive, booster, hot) differ in operational temperature during use of the igniter. None of the cited documents disclose operational performance of an igniter having more than two zones of differing resistivities as Appellant claims.

Claim 6 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the igniter of claim 5 wherein the hot zone has a higher operational temperature than the booster zone, and the booster zone has a higher operational temperature than the conductive zone. As discussed above, Axelson – the sole document relied on for a report of something analogous to Appellant’s claimed booster zone – is completely silent regarding any type of operational effects of an igniter having more than two zones of differing resistivities.

d) Claim 7

Claim 7 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the igniter of claim 1 wherein the booster operational temperature is about 200°C higher than the operational temperature of the conductive zone. None

of the cited documents disclose operational performance of an igniter having more than two zones of differing resistivities as Appellant's claim.

e) Claim 8

Claim 8 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the igniter of claim 1 wherein the booster operational temperature is at least about 100°C less than the operational temperature of the hot zone. None of the cited documents disclose operational performance of an igniter having more than two zones of differing resistivities as Appellant claims.

f) Claim 9

Claim 9 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the igniter of claim 1 wherein the room temperature resistance of the conductor zone is less than about 50 percent of the room temperature resistance of the booster zone. In the Final Office Action dated May 27, 2005, it is argued without any support from the prior art that resistance differences recited in claim 9 "are readily discoverable by routine experimentation by skilled artisans." Such an unsubstantiated allegation can not sustain a Section 103 rejection. See, for instance, MPEP §2143.03, as discussed above.

g) Claim 10

Claim 10 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the igniter of claim 1 wherein the room temperature resistance of the booster zone is less than about 70 percent of the room temperature resistance of the hot zone. In the Final Office Action dated May 27, 2005, it is argued without any support from the prior art that resistance differences recited in claim 10 "are readily discoverable by routine experimentation by skilled artisans." Such an unsubstantiated allegation can not sustain a Section 103 rejection. See, for instance, MPEP §2143.03, as discussed above.

h) Claim 11

Claim 11 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the igniter of claim 1 wherein the operational temperature resistivity of the booster zone is at least about 50 percent greater than the operational temperature resistivity of the hot zone. In the Final Office Action dated May 27, 2005, it is argued without any support from the prior art that resistivity differences recited in claim 11 “are readily discoverable by routine experimentation by skilled artisans.” Such an unsubstantiated allegation can not sustain a Section 103 rejection. See, for instance, MPEP §2143.03, as discussed above.

i) Claim 14

Claim 14 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest a method of igniting gaseous fuel comprising applying an electric current across an igniter an igniter of claim 1.

j) Claim 15

Claim 15 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the igniter of a method of claim 14 wherein the current has a nominal voltage of 6, 8, 10, 12, 24, 120, 220, 230 and 240 volts. Use of such voltages with the claimed igniters is demonstrated in the examples of the application and in the results disclosed in Dr. Yu’s Declaration.

k) Claim 16

Claim 16 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest a method of claim 14 or 15 wherein a hot zone of the igniter reaches at least about 1000°C within about one second of applying the current. Such fast time-to-temperature performance is specifically demonstrated in Example 2 of the present application as well as Dr. Yu’s Rule 132 Declaration.

l) Claim 17

Claim 17 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest a heating apparatus comprising an igniter of claim 1. As discussed above, igniters of the invention are particularly suited for use in a heating apparatus.

m) Claim 18

Claim 18 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest a heating apparatus of claim 17 that is an instantaneous water heater. The fast time-to-temperature performance of Appellant's preferred igniters render the igniters particularly suitable for use in an instantaneous water heater. See page 13, lines 28-30 of the application.

n) Claim 19

Claim 19 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest a heating apparatus of claim 17 that is a cooking apparatus.

o) Claims 21 and 22

Claims 21 and 22 each is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the igniter of claim 1 wherein the booster zone path length is from about 0.1 to about 2 cm as recited in claim 21, or a booster zone path length is from 0.2 to 1 cm as recited in claim 22. As discussed above, Axelson – the sole document relied on for a report of something analogous to Appellant's claimed booster zone – is silent regarding such zone length.

p) Claims 23 and 24

Claims 23 and 24 each is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the igniter of claim 1 wherein the igniter comprises a central heat sink zone. Axelson – the sole document relied on for a report of

something analogous to Appellant's claimed booster zone – does not mention use of a central heat sink.

q) Claim 25

Claim 25 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the igniter of claim 1 wherein the igniter has a time-to-temperature value of 2 seconds or less. Such fast time-to-temperature performance is specifically demonstrated in Example 2 of the present application as well as Dr. Yu's Rule 132 Declaration.

r) Claim 26

Claim 26 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest a sintered ceramic igniter element comprising a conductive zone, a power booster zone, and a hot zone,

the booster zone having a PTCR and a resistivity greater than the conductive zone and less than the hot zone,

the hot zone having a resistivity greater than the booster zone,

wherein the hot zone path length is 2 cm or less;

the igniter has a time-to-temperature value of 3 seconds or less;

the room temperature resistance of the conductive zone is less than about 50 percent of the room temperature resistance of the booster zone; and

the room temperature resistance of the booster zone is less than about 70 percent of the room temperature resistance of the hot zone.

As discussed above, the claimed booster zone resistance values as recited in claim 26 are described nowhere in any of the cited documents. The unsubstantiated allegation that such claimed features "are readily discoverable by routine experimentation by skilled artisans" is not a proper basis for rejection under 35 U.S.C. 103.

s) *Claim 27*

Claim 27 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the ceramic element of claim 26 wherein the igniter has a time-to-temperature value of 2 seconds or less. Such fast time-to-temperature performance is specifically demonstrated in Example 2 of the present application as well as Dr. Yu's Rule 132 Declaration.

t) *Claim 28*

Claim 28 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the sintered element of claim 26 wherein the room temperature resistance of the conductive zone is about 10 percent or less than the room temperature resistance of the booster zone. In the Final Office Action dated May 27, 2005, it is argued without any support from the prior art that resistance differences recited in claim 28 "are readily discoverable by routine experimentation by skilled artisans." Such an unsubstantiated allegation can not sustain a Section 103 rejection. See, for instance, MPEP §2143.03, as discussed above.

u) *Claim 29*

Claim 29 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the sintered element of claim 26 wherein the room temperature resistance of the booster zone is about 50 percent or less than the room temperature resistance of the hot zone. In the Final Office Action dated May 27, 2005, it is argued without any support from the prior art that resistance differences recited in claim 29 "are readily discoverable by routine experimentation by skilled artisans." Such an unsubstantiated allegation can not sustain a Section 103 rejection. See, for instance, MPEP §2143.03, as discussed above.

v) *Claim 30*

Claim 30 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest the sintered element of claim 26 wherein the igniter is

adapted for use at 6, 8, 10, 12 or 24 volts. Use of such voltages with the claimed igniters is demonstrated in the examples of the application and in the results disclosed in Dr. Yu's Declaration.

w) *Claim 31*

Claim 31 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest a method for igniting gaseous fuel, comprising applying an electric current across an igniter of claim 26, wherein the current has a nominal voltage of 6, 8, 10, 12 or 24 volts. Use of such voltages with the claimed igniters is demonstrated in the examples of the application and in the results disclosed in Dr. Yu's Declaration.

x) *Claim 32*

Claim 32 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest a method of claim 31 wherein the current has a nominal voltage of 24 volts. Indeed, comparative test results disclosed in Dr. Yu's Rule 131 Declaration (copy enclosed) include use of 24 volts.

y) *Claim 33*


Claim 33 is separately patentable for the above-stated reasons and further because the cited documents fail to teach or suggest a method of claim 31 wherein a hot zone of the igniter reaches at least about 1000°C within about one second of applying the current. Such fast time-to-temperature performance is specifically demonstrated in Example 2 of the present application as well as Dr. Yu's Rule 132 Declaration.

SUMMARY

Therefore, for the foregoing reasons, it is respectfully requested that the Board reverse the final rejection in this application.

Respectfully submitted,

Date: Oct. 14, 2006

By: 
Peter F. Corless (Reg. No. 33,860)
EDWARDS ANGELL PALMER & DODGE, LLP
P. O. Box 55874
Boston, MA 02205
Tel. (617) 439-4444
Fax (617) 439-4170 / 7748
Customer No.: 21874

CLAIMS APPENDIX A

Claim 1. A sintered ceramic igniter element comprising a conductive zone, a power booster zone, and a hot zone,
the booster zone having a PTCR and a resistivity greater than the conductive zone and less than the hot zone,
the hot zone having a resistivity greater than the booster zone,
wherein the hot zone path length is 2 cm or less and the igniter has a time-to-temperature value of 3 seconds or less.

Claim 2. An igniter element of claim 1 wherein the resistance of the booster zone permits i) current flow to the igniter hot zone and ii) resistance heating of the booster region during use of the igniter.

Claim 3. An igniter element of claim 1 or 2 wherein the resistance of the booster zone increases during application of current through the igniter and heating of the booster zone.

Claim 4. An igniter element of claim 1 wherein the igniter comprises in sequence the conductive zone, the booster zone and the hot zone.

Claim 5. An igniter of claim 1 wherein the three zones differ in operational temperature during use of the igniter.

Claim 6. An igniter element of claim 5 wherein the hot zone has a higher operational temperature than the booster zone, and the booster zone has a higher operational temperature than the conductive zone.

Claim 7. An igniter element of claim 1 wherein the booster operational temperature is about 200°C higher than the operational temperature of the conductive zone.

Claim 8. An igniter element of claim 6 or 7 wherein the booster operational temperature is at least about 100°C less than the operational temperature of the hot zone.

Claim 9. An igniter element of claim 1 wherein the room temperature resistance of the conductor zone is less than about 50 percent of the room temperature resistance of the booster zone.

Claim 10. An igniter element of claim 1 wherein the room temperature resistance of the booster zone is less than about 70 percent of the room temperature resistance of the hot zone.

Claim 11. An igniter element of claim 1 wherein the operational temperature resistivity of the booster zone is at least about 50 percent greater than the operational temperature resistivity of the hot zone.

Claim 14. A method of igniting gaseous fuel, comprising applying an electric current across an igniter of claim 1.

Claim 15. A method of claim 14 wherein the current has a nominal voltage of 6, 8, 10, 12, 24, 120, 220, 230 and 240 volts.

Claim 16. A method of claim 14 or 15 wherein a hot zone of the igniter reaches at least about 1000°C within about one second of applying the current.

Claim 17. A heating apparatus comprising an igniter of claim 1.

Claim 18. The apparatus of claim 17 wherein the apparatus is an instantaneous water heater.

Claim 19. The apparatus of claim 17 wherein the apparatus is a cooking apparatus.

Claim 21. The igniter of claim 1 wherein the booster zone path length is from about 0.1 to about 2 cm.

Claim 22. The igniter of claim 1 wherein the booster zone path length is from 0.2 to 1 cm.

Claim 23. The igniter of claim 1 wherein the igniter comprises a central heat sink zone.

Claim 24. The igniter of claim 23 wherein the igniter comprises a heat sink zone interposed between conductive, booster and hot zones of the igniter.

Claim 25. The igniter of claim 1 wherein the igniter has a time-to-temperature value of 2 seconds or less.

Claim 26. A sintered ceramic igniter element comprising a conductive zone, a power booster zone, and a hot zone,

the booster zone having a PTCR and a resistivity greater than the conductive zone and less than the hot zone,

the hot zone having a resistivity greater than the booster zone,

wherein the hot zone path length is 2 cm or less;

the igniter has a time-to-temperature value of 3 seconds or less;

the room temperature resistance of the conductive zone is less than about 50 percent of the room temperature resistance of the booster zone; and

the room temperature resistance of the booster zone is less than about 70 percent of the room temperature resistance of the hot zone.

Claim 27. The igniter element of claim 26 wherein the igniter has a time-to-temperature value of 2 seconds or less.

Claim 28. The igniter element of claim 26 wherein the room temperature resistance of the conductive zone is about 10 percent or less than the room temperature resistance of the booster zone.

Claim 29. The igniter element of claim 26 wherein the room temperature resistance of the booster zone is about 50 percent or less than the room temperature resistance of the hot zone.

Claim 30. The igniter element of claim 26 wherein the igniter is adapted for use at 6, 8, 10, 12 or 24 volts.

Claim 31. A method for igniting gaseous fuel, comprising applying an electric current across an igniter of claim 26, wherein the current has a nominal voltage of 6, 8, 10, 12 or 24 volts.

Claim 32. The method of claim 31 wherein the current has a nominal voltage of 24 volts.

Claim 33. The method of claim 31 wherein a hot zone of the igniter reaches at least about 1000°C within about one second of applying the current.

EVIDENCE APPENDIX B

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: C. Willkens

SERIAL NO.: 09/828,484

EXAMINER: J. Jeffrey

FILED: March 4, 2002

GROUP: 3742

FOR: CERAMIC IGNITERS

Commissioner For Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 CFR 1.132

I, Taehwan Yu declare as follows:

1. I received a Ph.D. in Materials Science and Engineering from the Massachusetts Institute of Technology in 1996. From the year 2000 to the present, I have been employed by the Saint-Gobain Corporation, and I have conducted research in the areas of the design and development of ceramic igniters throughout that employment. My present job title is Senior Research Engineer.

2. I am familiar with the above-identified application.

3. I conducted the following experimental work. A series of 24 volt sintered igniter elements having differing hot zone (resistive zone) lengths were evaluated to assess the effect of hot zone electrical path length relative to speed (i.e. time to specified ignition temperature after applying electrical input to the igniter) and temperature. These tested sintered igniters corresponded to the igniter disclosed in Example 1 of the above-identified application and were of the same composition and general dimensions, but had differing hot zone lengths as specified below.

4. More specifically, a series of sintered igniter elements corresponding to the igniter of Example 1 of the above-identified application and having differing resistive zone electrical path lengths were measured for their speed and resistance at 20.4V and temperature and amperage at temperature and amperage at 20.4V, 24V and 26V. Average values of measurements on the tested igniter elements from each tile are reported in Table 1 below. Speed was measured by time to temperature (TTT) to 1050°C at 20.4V. TTT of more than 10 seconds and temperatures of less than 800°C are reported as N/A as it exceeded the measurement capabilities. Figures 1 and 2 set forth below show the average electrical path length in hot zone relative to average speed (@20.4V) and temperature (@24V) for each tested igniter. TTT of 10 seconds and temperature of 0°C were assigned in the below Figures to the igniters exceeding the limit of measurement capabilities. Overall, there is a correlation of longer electrical path length with slower TTT and cooler temperature at the tip of the igniter element. Longer electrical path length increases the room temperature resistance and thus lowers in-rush current that is needed for rapid heating to ignition temperature. Additionally, longer electrical path length increased the overall volume of the resistive hot-zone further inhibiting rapid heating.

20.4V				24 V		26.4 V		Electrical path length
Temp °C	Amps (A)	TTT to 1050C (sec)	RTR (ohms)	Temp	Amps	Temp	Amps	(cm)
N/A	0.34	N/A	33.44	N/A	0.35	N/A	0.35	3.81
N/A	0.35	N/A	33.26	N/A	0.35	N/A	0.36	3.65
N/A	0.42	N/A	24.47	N/A	0.43	N/A	0.44	2.74
N/A	0.40	N/A	26.07	N/A	0.41	N/A	0.43	2.64
815	0.68	N/A	11.48	979	0.72	1062	0.76	1.16
776	0.64	N/A	13.49	951	0.68	1036	0.72	1.26
1135	1.07	4.25	6.07	1272	1.18	1346	1.28	0.45
1144	1.09	4.11	5.78	1283	1.20	1359	1.30	0.40
1216	1.31	2.41	5.74	1320	1.43	1383	1.55	0.35
1258	1.64	1.95	3.15	1349	1.79	1421	1.93	0.23
1268	1.63	1.85	3.26	1358	1.78	1435	1.91	0.15

Table 1. Average measured value of TTT (time to temperature to 1050°C) and RTR (room temperature resistance) at 20.4V and temperature and amperage at 20.4V, 24V and 26V for various electrical path lengths.

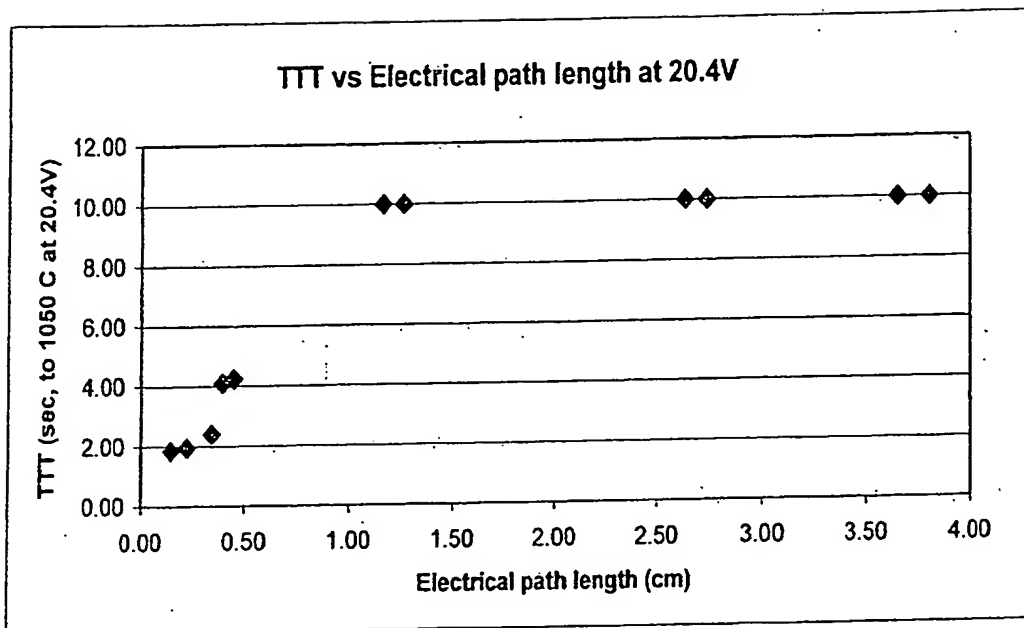


Figure 1. TTT vs. Electrical path length at 20.4V. Igniter elements with TTT of more than 10 seconds were assigned to 10 seconds in the figure.

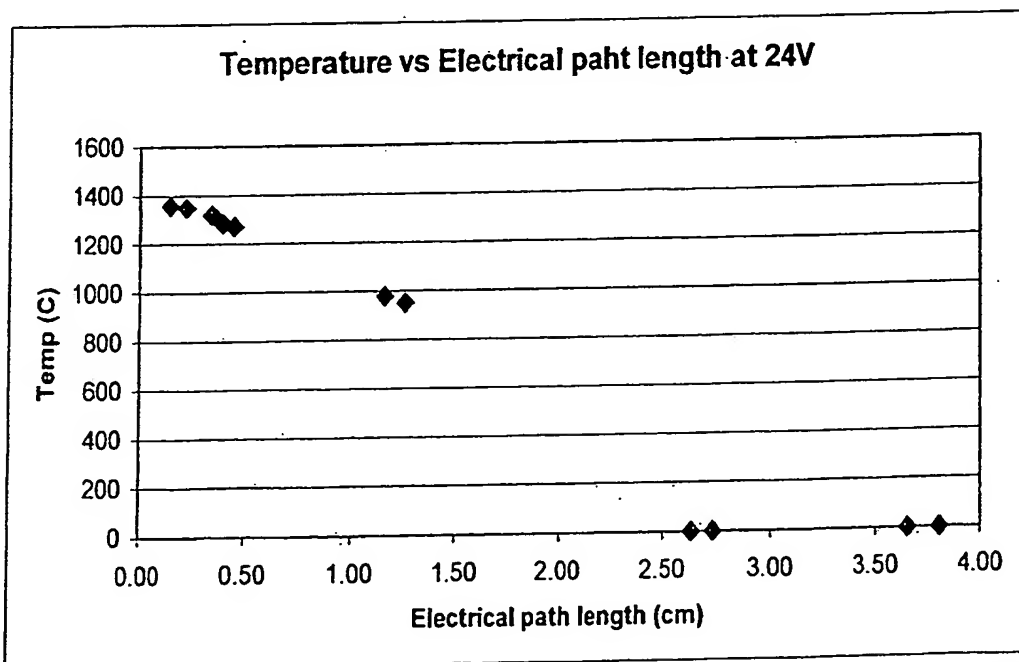



Figure 2. Temperature vs. Electrical path length at 24V. Elements with temperature of less than 800°C were assigned to 0°C in the figure.

5. The above results show that speed (i.e. time to targeted ignition temperature) decreases and temperature is reduced with increases in electrical path length of resistive hot zones of otherwise comparable igniter elements that have booster zone regions.

6. I hereby further declare that all statements made herein of my own knowledge are true and all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, and that such willful false statements may jeopardize the validity of the above-identified application or any patent issued thereon.

Date: _____

1-30-2004


Taehwan YU

PATENTS APPENDIX C



US005705261A

United States Patent [19]

Axelson

[11] Patent Number: **5,705,261**[45] Date of Patent: **Jan. 6, 1998**[54] **ACTIVE METAL METALLIZATION OF
MINI-IGNITERS BY SILK SCREENING**[75] Inventor: **Scott R. Axelson, Milford, N.H.**[73] Assignee: **Saint-Gobain/Norton Industrial
Ceramics Corporation, Worcester,
Mass.**[21] Appl. No.: **144,078**[22] Filed: **Oct. 28, 1993**[51] Int. Cl.⁶ **B32B 3/00; B32B 9/04;
B32B 9/00; H05B 3/10**[52] U.S. Cl. **428/210; 428/209; 428/446;
428/698; 428/699; 219/553; 373/117; 252/516;
501/91; 501/96**[58] Field of Search **428/210, 209,
428/446, 698, 699; 219/553; 373/117; 252/516;
501/91, 96**[56] **References Cited****U.S. PATENT DOCUMENTS**

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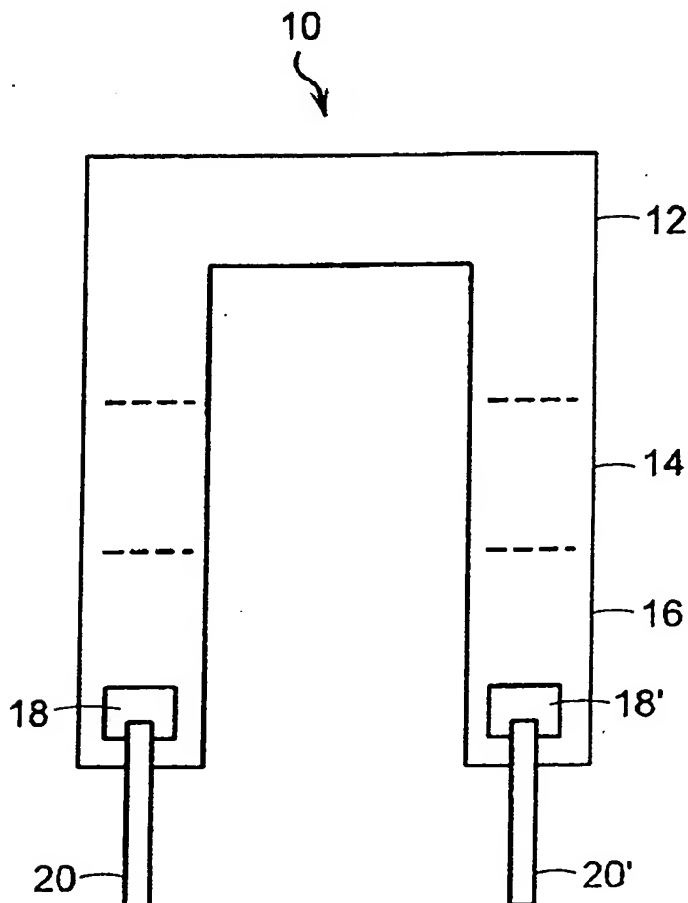
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Primary Examiner—Cathy F. Lam

Attorney, Agent, or Firm—Thomas M. DiMauro

[57] **ABSTRACT**

A ceramic igniter comprising: a) a lead wire, b) a ceramic substrate, and c) a braze pad having a thickness of less than about 150 microns, wherein the lead wire and ceramic substrate are placed in electrical connection by the braze pad.

12 Claims, 1 Drawing Sheet

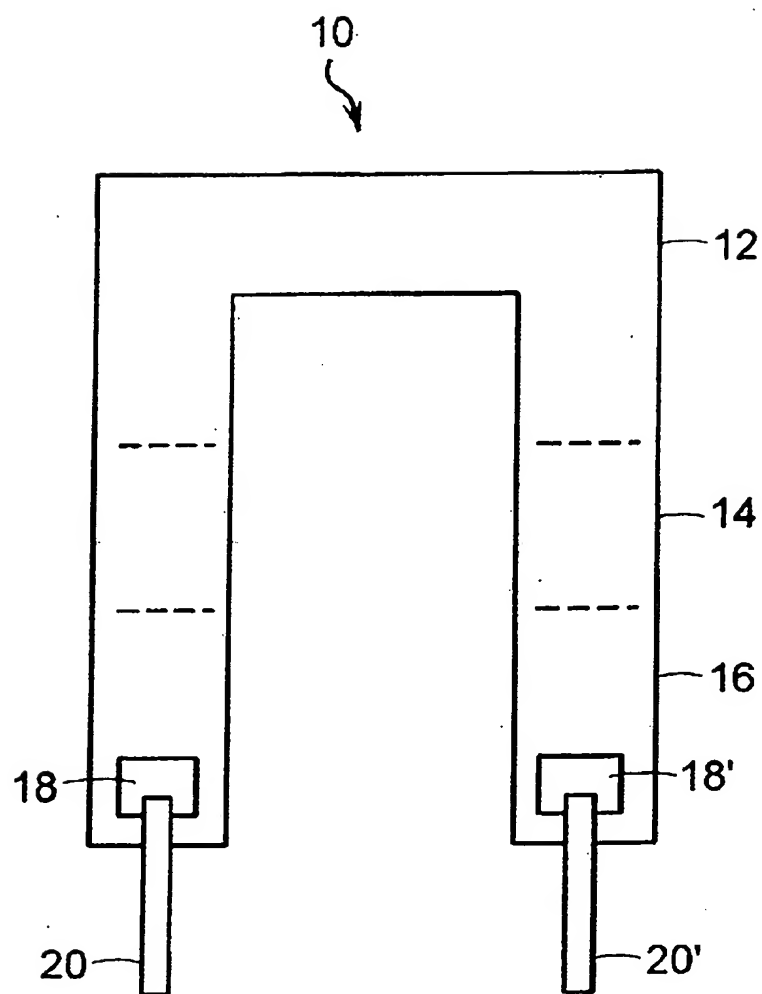


FIG. 1

ACTIVE METAL METALLIZATION OF MINI-IGNITERS BY SILK SCREENING

TECHNICAL FIELD

This invention relates to ceramic igniters and an improved method of making necessary electrical connections thereto. The improved electrical connections to the ceramic igniters are produced by silk screening a braze pad onto an electrically conductive portion of an igniter and then soldering an electrical lead wire to the braze pad. Careful silk screening provides good control of the braze pad thickness. Thin braze pads so produced are less affected by thermal shock and so are less prone to cause thermal expansion-induced fracture of the ceramic.

BACKGROUND OF THE INVENTION

Although ceramic igniters have been known and commercially used for many years, the art has been plagued by in-service resistivity increases as well as premature failure of the igniters' electrical connections. Ceramic igniter production requires constructing an electrical circuit through a ceramic component, a portion of which is highly resistive and thus rises in temperature when current is run through it from an electrical lead. However, the conductive interface between the electrical lead and the ceramic typically experiences dissimilar thermal expansion effects from the lead and the ceramic and so is susceptible to cracking. Further, undesired highly resistive zones are often created by either reaction between the metal lead and the ceramic, any other chemical interaction used in forming the combined mechanical and electrical connection, mechanical failure or chemical deterioration, i.e., oxidation. Such large increases in resistance are a problem because an igniter must be capable of igniting fuel gases throughout the lifetime of an appliance, even when voltages sink as low as 85% of the standard operating voltage (i.e., 20.4 V instead of 24.0 V) during brownouts or peak electrical demand periods. When the available voltage decreases significantly, an insufficient igniter temperature may result, particularly in older igniters in which the electrical contact has experienced severe deterioration. Hence, achieving both consistent resistivity and electrical continuity has been a continuing goal in this field.

Previous attempts at making electrical connections for ceramic igniters have had varied results. For example, U.S. Pat. No. 3,875,477 discloses a process involving (i) lightly sandblasting portions of a silicon carbide igniter in the areas where the electrical contacts are to be made, (ii) coating the sandblasted terminal ends with aluminum metal or an aluminum alloy either by dipping into molten metal or by flame spraying, and (iii) using a refractory, electrically insulating cement of the high alumina type. U.S. Pat. No. 3,928,910 discloses gas igniters having electrical leads bonded into physical slots of a ceramic (SiC) body by high temperature flame or plasma spraying which is not only intended to secure the inserted leads into their respective slots but also to fully and continuously encase the terminal parts of the igniter. U.S. Pat. No. 5,045,237 discloses molybdenum disilicide-containing ceramic igniters in which a simple machine screw and nut assembly is placed through machined holes in the ceramic body. However, the above connection means in each of these references has suffered from the problem of either substantially increased resistance with extended use, i.e., at least about a 5% increase after 100,000 on/off cycles, or failing to be commercially reproducible.

The Norton Company of Worcester, Mass. has produced ceramic igniters in which the electrical contacts have less

than about a 2% change in contact resistance after 100,000 on/off cycles. These igniters are prepared by (i) forming a ceramic igniter body having a molybdenum disilicide content of at least about 20 volume percent at the points at which the electrical contacts are to be made, (ii) painting an active metal braze on the body at those points, and (iii) soldering electrical leads to said pads by means of a solder which melts at a temperature of greater than about 500° C. However, thermal expansion mismatch between the braze and the ceramic often produces cracking in the braze, leading to failure of the electrical connection.

Accordingly, it is the object of the present invention to produce a commercially viable improved ceramic igniter which

- (i) will maintain a desired contact resistance after significant use, and
- (ii) has the desired thermal expansion characteristics in the braze.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a ceramic igniter comprising:

- a) a lead wire,
- b) a ceramic substrate, and
- c) a braze pad having a thickness of less than about 150 microns,

wherein the lead wire and ceramic substrate are placed in electrical connection by the braze pad.

Also in accordance with the present invention, there is provided a process for making an improved ceramic igniter comprising an electrically conductive ceramic substrate, comprising the steps of:

- (a) silk screening a braze material onto the electrically conductive ceramic substrate to produce a braze pad, and
- (b) soldering an electrical lead to said braze pad by means of a solder which melts at a temperature of at least about 500° C.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a top view of a preferred igniter body with connecting leads soldered to braze pads in accordance with this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Without wishing to be tied to a theory, it is believed that the conventional method of painting the braze onto the ceramic substrate deposited more braze than was needed to make the required electrical contact. The volume changes experienced by this excessive braze during temperature swings is believed to be enough to cause the fracture of the ceramic under the braze and the failure of the circuit. Such temperature swings are believed to occur during construction of the igniter and during use. By silk screening the braze onto the ceramic in a highly controlled manner, the braze can be tailored to sufficiently thin and narrow dimensions, thereby preventing the deposition of the excessive braze and avoiding thermal expansion-induced fracture of the braze pad and failure of the electrical connection. Accordingly, the igniters of the present invention not only maintain the desired long term contact resistance (due to the use of a braze) but also have the desired thermal expansion characteristics (due to the thin depth of the braze).

The silk screening of the braze onto the ceramic may be accomplished by any conventional silk screening method. In one embodiment, a Model #SP-SA-5 silk screen unit, available from deHaart, Inc. of Burlington, Mass., is used. When this unit is used, however, it must first be initialized with reference to the ceramic igniter in order to assure proper registration of the braze pattern on the igniter. In one initialization procedure, a brass nest, available from Hermetic, Inc. of Burlington, Mass., is mounted on a vacuum base plate on the printing table of the unit. Ultrasonically cleaned igniter elements are then placed on the table and held in place either via a vacuum or with light adhesive tape. Concurrently, a polymer mesh screen, available from RIV Inc. of Merrimac, N.H., is mounted on the underside of a squeegee frame, which is then lowered into screening position in the unit in order to set the height between the screen and the igniters in the fixture. A feeler gauge is used to first adjust the separation distance to about 0.0015 inches (38.1 microns). This distance is then set back an additional 0.020 inches (508 microns) to allow for screen snapback. The squeegee pressure is set for about 20 psi downforce. The screen is then removed from the frame to set the squeegee-nest fixture separation. The front application squeegee is adjusted for about 0.001 inch separation (25.4 microns) while the rear application squeegee is adjusted for about 0.016 inch separation (406.4 microns), both being set by a feeler gauge and micrometer dial. The screen is then reinstalled on the squeegee frame. The registration of the screen pattern with the elements in the nesting fixture is then set using the x-y axis micrometer dial adjustments on the printing table. Igniter blanks are placed in the fixture and braze paste having a suitable viscosity for screening is applied to the screen with a spatula. The unit is then turned on and the braze is applied to the igniter blanks. The blanks are then inspected visually and x-y adjustment is made to center the metallization on the igniter leg, preferably to within about 0.25 inches (6350 microns) of the end of the leg. This process is then repeated until the proper registration is achieved.

A braze pad produced from the silk screening process of the present invention typically has a thickness of less than about 150 microns, preferably less than about 115 microns, more preferably less than about 80 microns. Without wishing to be tied to a theory, this reduced-thickness pad lessens the thermal expansion response of the braze pad during periods of thermal shock.

The pads typically have an exposed surface area of less than about 3.6 square millimeters, preferably less than about 2.6 square millimeters and more preferably less than about 2.2 square millimeters. In practice, it has been found that the exposed surface area of the braze pad should be as small as possible and centered on the end of the igniter leg in order to insure that the pad is not contacting machining edge flaws left from the ceramic element manufacturing process.

The braze composition used with the present invention may be any braze composition conventional in the art which forms an electrical connection with the highly conductive portions of the ceramic igniter. To obtain the required high degree of adhesion to the ceramic, the braze typically contains an active metal which can wet and react with the ceramic materials and so provide adherence thereto by filler metals contained in the braze. Examples of specific active metals include titanium, zirconium, niobium, nickel, palladium, and gold. Preferably, the active metal is titanium or zirconium. In addition to the active metal, the braze contains one or more filler metals such as silver, copper, indium, tin, zinc, lead, cadmium, and phosphorous. Prefer-

ably a mixture of filler metals is used. Most preferably, the braze will comprise titanium as the active metal and a mixture of copper and silver as the filler metal. Generally, the braze will contain between about 0.1 and about 5 weight percent ("w/o") active metal and between about 99.9 and about 95 w/o filler metal. Such suitable brazes are commercially available under the trade name Lucanex from Lucas-Milhaupt, Inc. of Cudahy, Wis., and Cusil and Cusia from Wesgo, Inc. of Belmont, Calif. Specific brazes found useful with the present invention include: Lucanex 721 and Cusil Braze, each of which contains about 70.5 w/o silver, about 27.5 w/o copper, and about 2 w/o titanium.

The ceramic portion of the present invention may be any ceramic commonly used in the igniter field. Preferably, the ceramic comprises aluminum nitride, molybdenum disilicide, and silicon carbide. More preferably, a mixture of aluminum nitride (AlN), molybdenum disilicide (MoSi₂) and silicon carbide (SiC), as disclosed in U.S. Pat. No. 5,045,237 ("the Washburn patent"), the specification of which is wholly incorporated by reference herein, is used.

The igniter preferably comprises about 40 to 70 volume percent ("v/o") of a nitride ceramic and about 30 to 60 v/o MoSi₂ and SiC in a volume ratio of from about 1:3 to 3:1. A more preferred igniter has a varying composition as described by the Washburn patent. FIG. 1 presents an igniter of the present invention wherein the chemical composition of the igniter 10 is varied from a highly resistive portion 12 through an intermediate portion 14 to a highly conductive portion 16. Preferably, however, the intermediate portion 14 is omitted for ease of manufacturing. The igniter is also provided with the two active metal braze pads 18 and 18' to which electrical leads 20 and 20' are respectively soldered in accordance with this invention.

The highly resistive portion 12 generally has a resistivity of at least about 0.04 ohm-cm, preferably at least about 0.07 ohm-cm in the temperature range of 1000° to 1600° C. It preferably comprises about 50 to 70 v/o nitride ceramic and about 30 to 50 v/o MoSi₂ and SiC in a volume ratio of about 1 part MoSi₂ about 2 parts SiC.

The intermediate portion 14, when present, preferably comprises about 50 to 70 v/o nitride ceramic and about 30 to 50 v/o MoSi₂ and SiC in a volume ratio of about 1:1.

The highly conductive portion 16 generally has a resistivity of less than about 0.005 ohm-cm, preferably less than about 0.003 ohm-cm, and most preferably less than about 0.001 ohm-cm in the temperature range of 100° to 800° C. It preferably comprises about 30 to 55 v/o nitride ceramic and about 45 to 70 v/o MoSi₂ and SiC in a volume ratio of from about 1:1 to about 2:3.

Suitable nitrides for use as the resistive component of the ceramic igniter include silicon nitride, aluminum nitride, boron nitride, and mixtures thereof. Preferably the nitride is aluminum nitride.

Electrical wire leads of the present invention are conventionally connected to the braze pads by a solder. The solder should be able to withstand temperatures of about 485° C. during use without degradation and also must have low resistivity. Generally, a solder having a melting point of above about 500° C., and preferably above about 600° C. is used. Suitable solders typically contain the following compounds in w/o:

	Typical Embodiment	Preferable Embodiment	More Preferable Embodiment
Silver	1-90	10-70	15-60
Copper	5-80	10-70	10-60
Zinc	5-40	10-35	12-30
Other Metals	0-40	0-30	0-30

The "Other Metals" described above include one or more metals selected from aluminum, tin, indium, phosphorous, cadmium, and nickel. Suitable solders are commercially available under the trade name Safety-Silv from J. W. Harris Co., Inc. of Cincinnati, Ohio. A specific solder found useful herein is Safety-Silv 45 which nominally contains 45 w/o silver, 30 w/o copper, and 25 w/o zinc. Other specific solders which may be used include Safety-Silv 1200, which nominally contains 56% silver, 22% copper, 17% zinc, and 5% tin, and Safety-Silv 1577 which nominally contains 25% silver, 52.5% copper, and 22.5% zinc.

In soldering the lead wires to the braze pads, it has been found advantageous to introduce the solder directly to the wire-braze pad interface (coated with flux). When a torch is applied to heat the interface, the solder flows onto the wire and onto the brazed region to make a strong, conductive join. In some embodiments, an oxy-acetylene torch is used as the heat source. In other embodiments, a Microflame soldering head system utilizing hydrogen, available from mta/Schunk Automation of Old Saybrook, Conn., is used.

After the igniters are silk screened, they are fired, typically in a graphite fixture, in order to fuse the braze to the ceramic. Generally, the igniters are fired at between about 810° and about 890° C. for about 6-10 minutes in a furnace having a pressure of less than about 0.0001 torr. Alternatively, they may be fired in a continuous belt furnace having an argon atmosphere with a concentration of less than about 50 ppm oxygen.

The igniters of the present invention may be used in many applications, including gas phase fuel ignition applications such as furnaces and cooking appliances. The practice of the present invention can be further appreciated from the following non-limiting Examples and Comparative Examples.

EXAMPLE 1

A double-legged hairpin ("U-shaped") ceramic igniter as shown in FIG. 1 was prepared from aluminum nitride, silicon carbide, and molybdenum disilicide in accordance with the teachings of the Washburn patent. The composition of the ceramic, in v/o, was as follows:

	Aluminum Nitride	Molybdenum Disilicide	Silicon Carbide
Conductive portion	50	30	20
Resistive portion	60	13	27

Next, an active metal brazing paste, Lucanex 721, manufactured by Lucas-Mihaupt, was heated by means of a refractory metal furnace under a high vacuum to a temperature of 875° C. for about 6 minutes in order to fuse the metal powder braze and chemically react it with the ceramic substrate. The braze was then silk screened onto a 1000 umx2500 um area of each of the legs to form a pad having a thickness of about 150 microns.

To adhere a conventional copper electrical wire to each of the braze pads, Safety-Silv 45 solder is used. The soldering was performed using an oxy-acetylene torch as a heat

source. The solder wire was dipped in a standard silver solder flux to flow into the join and clean the surfaces to be joined, allowing the silver solder to melt and flow into the braze pad-wire interface. The heat was removed and the join was held in place for an additional 5 seconds until the solder hardened by cooling.

The ceramic igniters produced by this process were then examined by visual and 20X binocular microscope for cracks in the braze pad. It was observed that less than about 0.4% of the braze pads had cracks.

COMPARITIVE EXAMPLE I

The procedure of Example 1 is repeated identically, except that the braze is merely brushed onto the ceramic substrate. The resulting pad had a thickness of about 200 microns and an area of about 9.0 square millimeters.

The ceramic igniters produced by this process were then examined as above for cracks in the braze pad. It was observed that more than about 30% of the braze pads had cracks. It is believed these cracks are due to the braze pads a volume expansion caused by thermal shock from the heating required in the soldering process.

What is claimed is:

1. A ceramic igniter comprising:

a) a ceramic substrate having first and second conductive ends and a highly resistive middle portion, the conductive ends comprising between 30 volume percent and 55 volume percent nitride ceramic, and

b) a braze pad disposed on each conductive end of the ceramic substrate, each pad having a thickness of less than about 150 microns, the braze pad comprising between about 95 weight percent and about 99.9 weight percent of at least one filler metal selected from the group consisting of silver, copper, indium, tin, zinc, lead, cadmium and phosphorous.

2. The igniter of claim 1 wherein each pad has a thickness of less than about 115 microns.

3. The igniter of claim 1 wherein each pad has a thickness of less than about 80 microns.

4. The igniter of claim 1 wherein the conductive ends further comprise between about 45 volume percent and 70 volume percent molybdenum disilicide and silicon carbide.

5. The igniter of claim 4 wherein the braze pad further comprises between about 0.1 and about 5 weight percent of an active metal selected from the group consisting of titanium, zirconium, niobium, nickel, palladium and gold.

6. The ceramic igniter of claim 1 wherein the braze pad comprises titanium, copper and silver.

7. The igniter of claim 1 further comprising:

c) a lead wire disposed on each braze pad.

8. The igniter of claim 7 further comprising: d) a solder which bonds the lead wire to its corresponding braze pad, wherein the solder has a melting point of at least 500° C.

9. The igniter of claim 1 wherein each pad has an exposed surface area of less than about 3.6 square millimeters.

10. The igniter of claim 5 wherein each pad has an exposed surface area of less than about 2.6 square millimeters.

11. The igniter of claim 4 wherein the molybdenum disilicide and silicon carbide are present in the conductive ends in a volume ratio of from about 1:1 to about 2:3.

12. The igniter of claim 8 having no interlayer between the braze pad and the solder.



US005786565A

United States Patent [19]

Willkens et al.

[11] Patent Number: 5,786,565

[45] Date of Patent: Jul. 28, 1998

[54] MATCH HEAD CERAMIC IGNITER AND METHOD OF USING SAME

[75] Inventors: Craig A. Willkens, Worcester; Linda S. Bateman, Spencer, both of Mass.

[73] Assignee: Saint-Gobain/Norton Industrial Ceramics Corporation, Worcester, Mass.

[21] Appl. No.: 789,033

[22] Filed: Jan. 27, 1997

[51] Int. CL⁶ F23Q 7/00; F23Q 7/22; H05B 3/10

[52] U.S. Cl. 219/260; 219/270; 219/542; 219/548; 252/516

[58] Field of Search 219/260, 267, 219/270, 538, 539, 542, 543, 544, 546, 548, 552, 553; 252/516, 518; 501/89, 92, 96.3, 97.4, 98.6

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3,875,477 4/1975 Fredriksson et al. 219/553
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5,085,804 2/1992 Washburn 252/516
 5,191,508 3/1993 Axelson et al. 361/257
 5,514,630 5/1996 Willkens et al. 501/89
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Primary Examiner—Tu B. Hoang

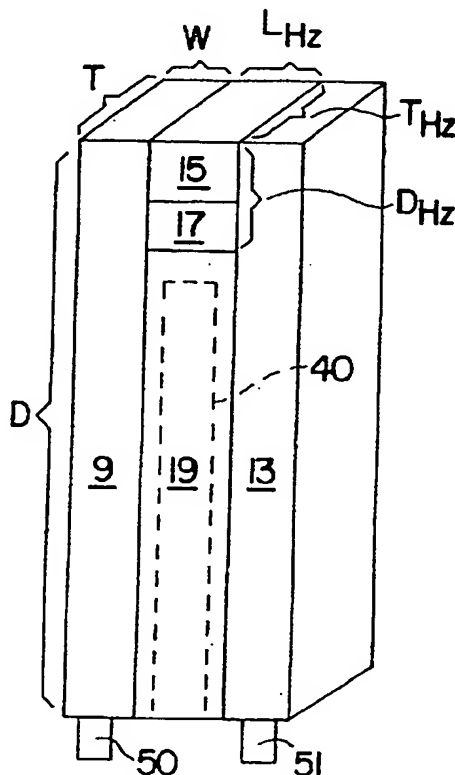
Attorney, Agent, or Firm—Thomas M. DiMauro

[57] ABSTRACT

A ceramic igniter comprising:

- a) a pair of electrically conductive portions, each portion having a first end,
- b) a hot zone disposed between and in electrical connection with each of the first ends of the electrically conductive portions, the hot zone having an electrical path length of less than 0.5 cm. and
- c) an electrically non-conductive heat sink material contacting the hot zone.

24 Claims, 5 Drawing Sheets



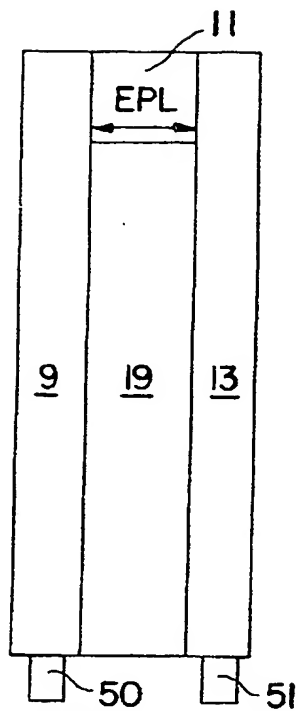


FIG. 1

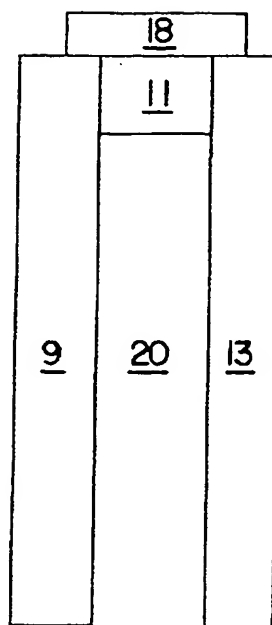


FIG. 2

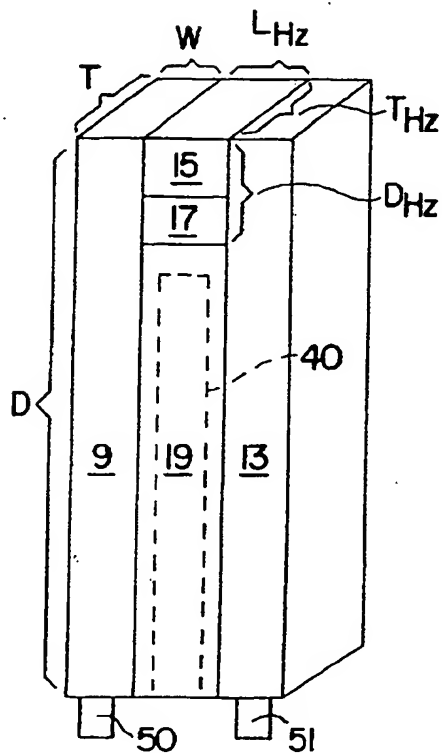


FIG. 3

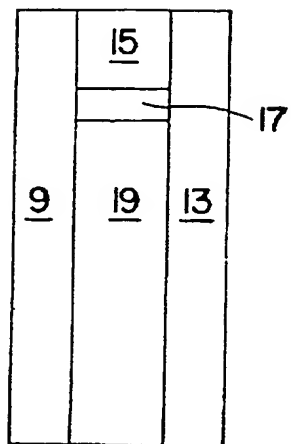


FIG. 4

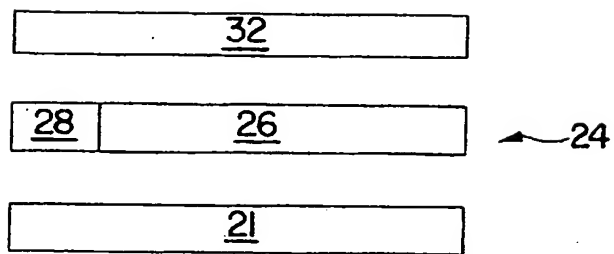


FIG. 5

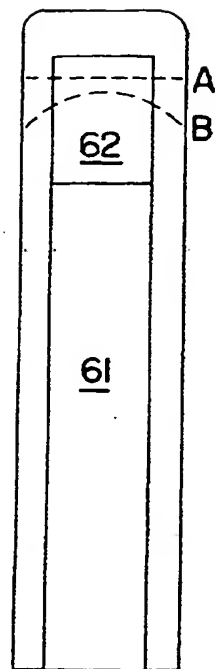


FIG. 6

FIG. 7

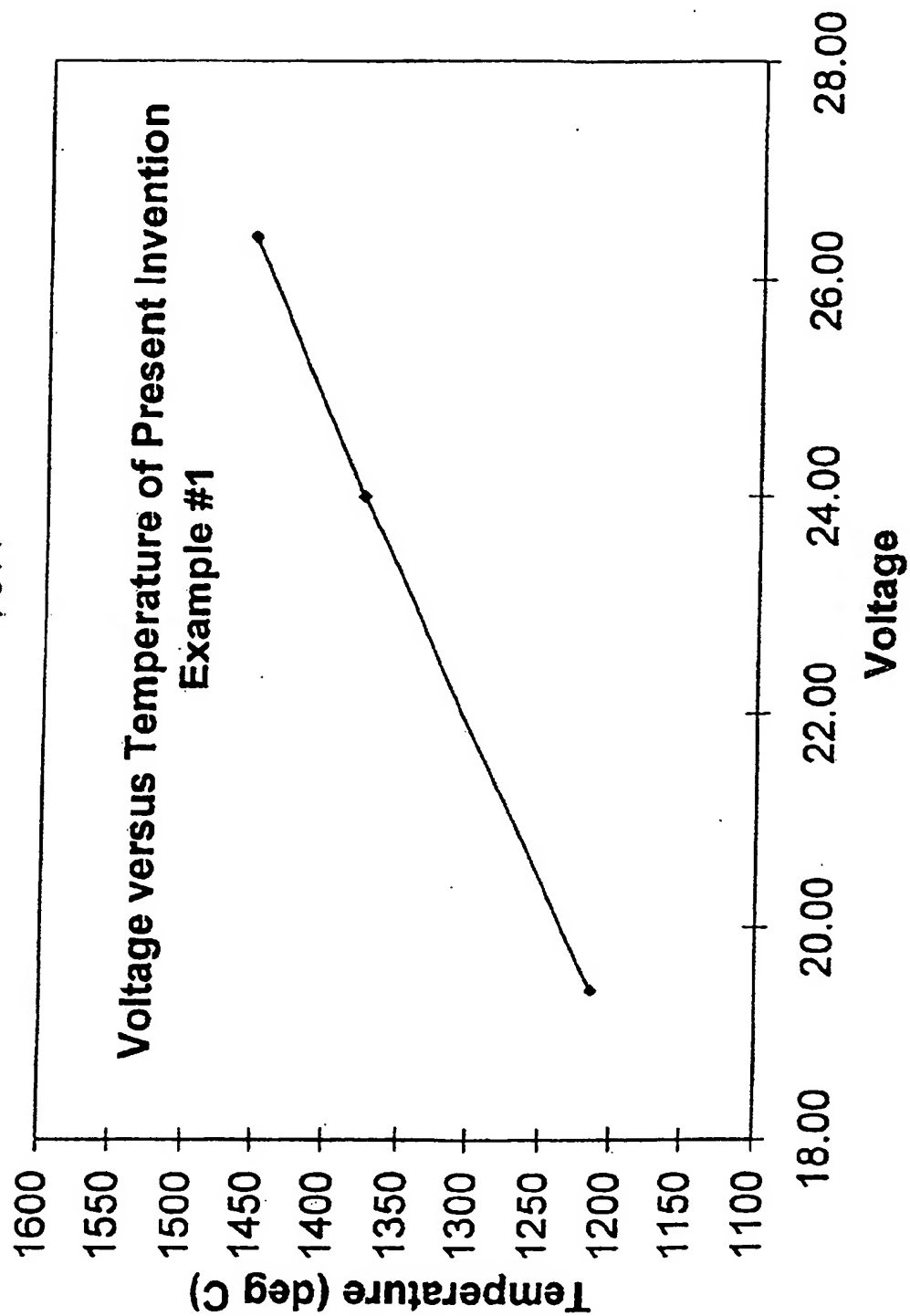


FIG. 8A

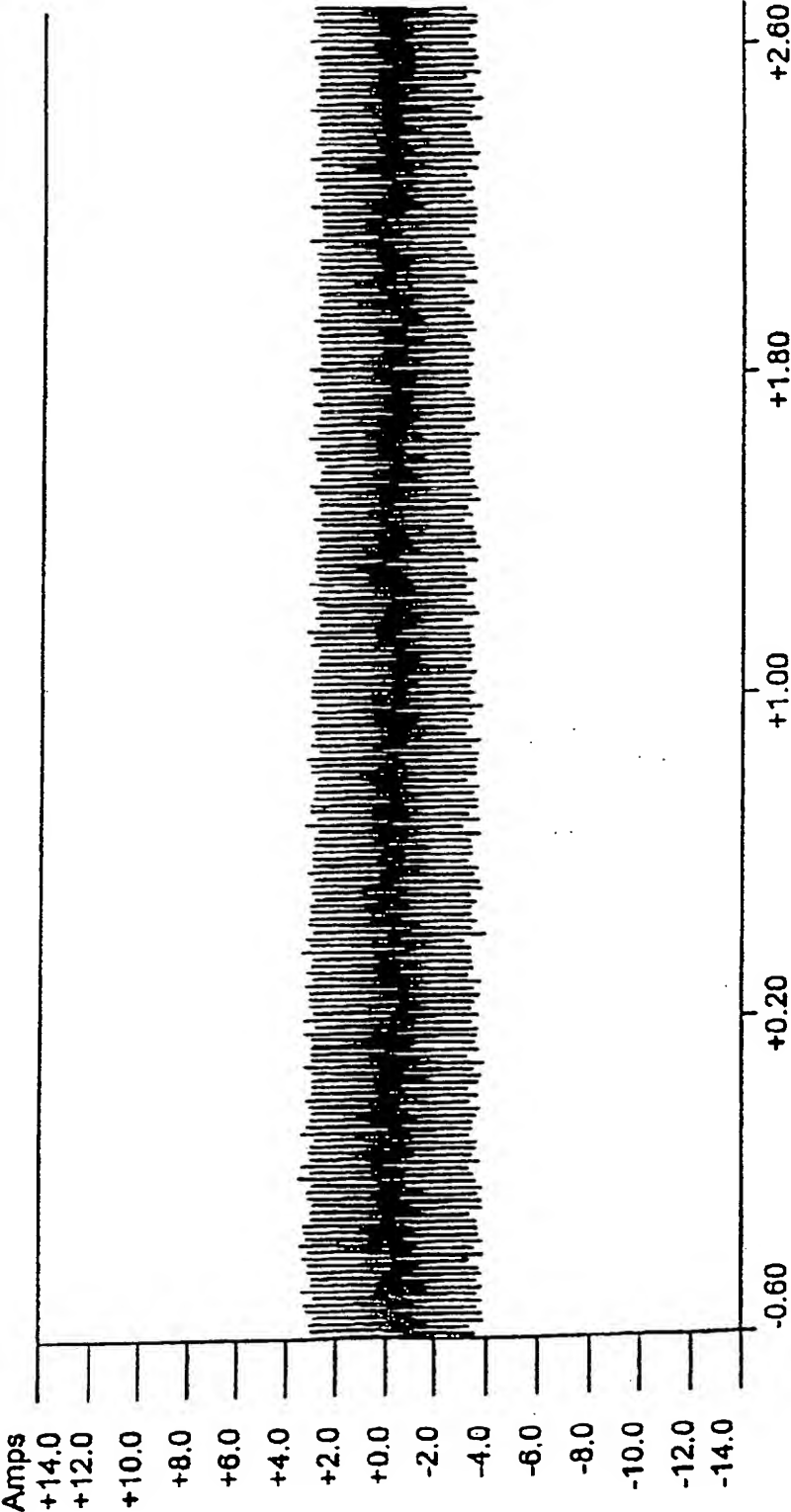
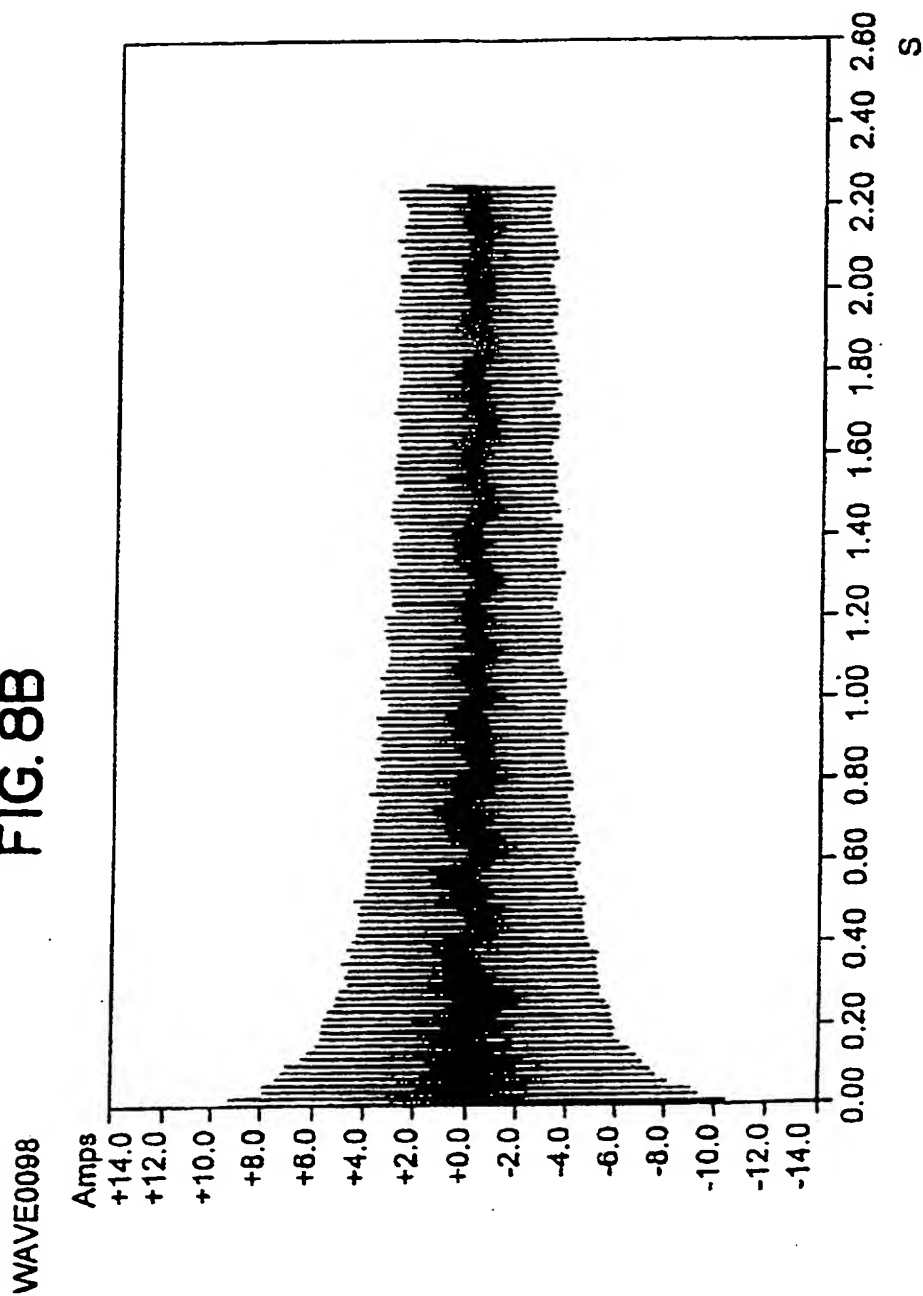


FIG. 8B



MATCH HEAD CERAMIC IGNITER AND METHOD OF USING SAME

BACKGROUND OF THE INVENTION

Ceramic materials have enjoyed great success as igniters in gas fired furnaces, stoves and clothes dryers. A ceramic igniter typically has a hair-pin shape which contains conductive end portions and a highly resistive middle portion. When the igniter ends are connected to electrified leads, the highly resistive portion (or "hot zone") rises in temperature. Some of these igniters must meet the following requirements set by the appliance and heating industries to anticipate variations in line voltage:

Time to design temperature	<5 sec
Minimum temperature at 85% of design voltage	1100° C.
Design temperature at 100% of design voltage	1350° C.
Maximum temperature at 110% of design voltage	1500° C.
Hot-zone Length	<1.5"
Power (W)	65-100.

U.S. Pat. No. 5,085,804 ("the '804 patent") along with companion U.S. Pat. No. 5,405,237 disclose compositions suitable for a hot zone of a ceramic igniter, the hot zone comprising:

- between 5 and 50 v/o MoSi₂, and
- between 50 and 95 v/o of a material selected from the group consisting of silicon carbide, silicon nitride, aluminum nitride, boron nitride, aluminum oxide, magnesium aluminate, silicon aluminum oxynitride, and mixtures thereof. According to the '804 patent, these compositions provide the proper speed, room temperature resistivity and high temperature resistivity required for attaining the above-noted requirements without constraining the shape of the igniter.

One conventional igniter, the Mini-Igniter™, available from the Norton Company of Milford, N.H., uses a hot zone composition from the '804 patent which comprises aluminum nitride ("AlN"), molybdenum disilicide ("MoSi₂"), and silicon carbide ("SiC") and a total hot zone length of between about 1.5 cm (for 12V applications) and 6 cm (for 120 V applications). Although the Mini-Igniter™ performs well in many applications, its speed (i.e., the time it takes to heat up from room temperature to the 1350° C. design temperature) is typically between 3 and 5 seconds (for 24V to 120V applications). It is believed the applicability of these igniters could be greatly expanded if their speed could be decreased below 3 seconds.

Attempts have been made to increase the speed of these igniters. For example, Washburn and Voeller, "Low Power Gas Ignition Device, presented in the Proceedings of the 1988 International Appliance Technical Conference—Europe" (1988), pp.134-149, discloses achieving speeds as low as 1.5 seconds by reducing the mass of the hot zone to about 0.07 to 0.08 grams (i.e., a length of about 1.0 cm to 1.3 cm). However, it is believed these igniters would be very susceptible to blowout caused by convective cooling. Willkens et al. "High Voltage Miniature Igniter Development", International Appliance Technical Conference, Madison, Wis. (1994) advise designing the length of the hot zone to be at least 0.7 inches (1.8 cm) for a 120V igniter. The '804 patent also advises providing a hot zone length of at least 0.2 inches (or about 0.5 cm) as a practical minimum limit.

In addition, these igniters generally experience a very high in-rush current (i.e., a current of about 10 amperes in the first millisecond) before settling down to a conventional 2 to

3 ampere current. Since any transformer designed for use with these igniters must be designed to accept this initial high current, these igniters must be paired with a transformer capable of receiving higher power instead of the less costly transformer rated for a lower power.

Simply lowering the resistivity of the hot zone composition (by increasing its conductive MoSi₂ content) has been considered as a method of increasing the speed of the igniter. However, it was found that doing so increases the inrush current to even higher levels (due to a lower room temperature resistivity) and makes the igniter prone to burnout due to unacceptably high power levels for the typical igniter geometry. These igniters are unable to radiate energy sufficiently to produce a stable temperature.

Similarly, raising the resistivity of the hot zone composition (by decreasing its MoSi₂ content) has been considered as a method of decreasing the inrush current of the igniter. However, it was found that doing so not only decreased the speed of the igniter (due to a higher room temperature resistivity), it also provided an unstable igniter at high temperatures (due to its negative temperature coefficient of resistance at high temperature).

Therefore, there is a need for a ceramic igniter which has high speed but also resists cooling effects, and which has a low inrush current.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a ceramic igniter comprising:

- a pair of electrically conductive portions, each portion having a first end,
- a resistive hot zone disposed between and in electrical connection with each of the first ends of the electrically conductive portions, the hot zone having an electrical path length of less than 0.5 cm, and
- an electrically non-conductive heat sink material contacting the hot zone.

For the purposes of the present invention, the "electrical path length" is the shortest path taken by an electrical current through the hot zone when an electrical potential is applied to the conductive ends of the igniter.

Also in accordance with the present invention, there is provided a method of heating, comprising the steps of:

- providing a ceramic igniter comprising:
 - a pair of electrically conductive portions, each portion having a first end,
 - a resistive hot zone disposed between and in electrical connection with each of the first ends of the electrically conductive portions, the hot zone having an electrical path length of no more than 0.5 cm, and
 - an electrically non-conductive heat sink material contacting the hot zone,
- applying a voltage of between 3 V and 60 V between the conductive ends of the igniter to produce an inrush current and a steady state current such that the ratio of the steady state current to the inrush current is at least 35% (preferably at least 50%), and raising the temperature of the hot zone to about 1350° C. in less than 3 seconds (preferably less than 2 seconds).

DESCRIPTION OF THE FIGURES

FIG. 1 is a cross-sectional view of a preferred embodiment of the present invention, wherein the electrically insulating heat sink is disposed as an insert between the conductive legs of the igniter.

FIG. 2 is a cross-sectional view of a preferred embodiment of the present invention, wherein the electrically insulating heat sink contacts the opposing side of the hot zone.

FIG. 3 is a perspective view of a preferred igniter of the present invention.

FIG. 4 is a cross-sectional view of an igniter of the present invention wherein the hot zone comprises two resistive sections.

FIG. 5 displays an exploded view of a preferred green body of the present invention.

FIG. 6 is a cross section view of an igniter of the present invention made with tape cast conductive legs.

FIG. 7 displays the electrical performance of Example I in terms of voltage and temperature. FIGS. 8a and 8b display the inrush amperage over time for the igniter of the present invention (8a) and the prior art igniter (8b).

DESCRIPTION OF THE INVENTION

It has been found that decreasing the hot zone electrical path length to less than 0.5 cm and contacting the hot zone with an electrically insulating heat sink material produces a commercially acceptable igniter which has high speed, high resistance to convective cooling, and a low inrush current. Moreover, when electronics or transformers are used to lower the effective voltage seen by the igniter, the lower inrush current of the present invention lessens the need for such extensive and expensive modifications.

Without wishing to be tied to a theory, it is believed the added thermal mass of the heat sink significantly slows convective cooling of the hot zone, thereby allowing the hot zone to remain hot under convective cooling conditions despite its small length.

In preferred embodiments, the igniter has a hairpin configuration comprising two parallel conductive legs and a connecting hot zone bridge positioned therebetween, with the remaining space between the legs being at least partially filled by an electrically insulating heat sink material such as aluminum nitride which contacts the hot zone. For example, as shown in FIG. 1, one preferred igniter of the present invention has a hairpin shape comprising two conductive legs 9 and 13 placed in electrical connection by a resistive hot zone 11, the legs 13 extending from the hot zone in the same direction.

The electrical path length of the hot zone, shown as EPL in FIG. 1, is less than 0.5 cm. Insulating heat sink material 19 is provided as an insert to contact the hot zone and substantially fill the remaining space between the conductive legs extending from the hot zone 11. When paired leads 50 and 51 are attached to each of the conductive ends 9 and 13 and a voltage is applied thereto, current travels from the first lead 50 to first conductive leg 9, through the hot zone 11 (thereby causing the temperature of the hot zone to rise), and then through the second conductive leg 13 where it exits through the second lead 51.

In other embodiments, the electrically insulating heat sink material can contact other surfaces of the hot zone. As in FIG. 2, the electrically insulating heat sink material 18 contacts hot zone 11 on the opposing side of the space 20 created between the parallel conductive legs 9 and 13. This design still provides the heat sink contact desirable for high speeds and low in-rush current without altering the electrical characteristics of the igniter.

Typically, the hot zone has a high temperature (i.e., 1350° C.) resistivity of between about 0.001 ohm-cm and about 3.0

ohm-cm, a room temperature resistivity of between about 0.01 ohm-cm and about 3 ohm-cm, and is usually characterized by a positive temperature coefficient of resistance ("PTCR"). In preferred embodiments, the hot zone comprises a first resistive material comprising:

- (a) between about 50 and about 75 vol % of an electrically insulating material selected from the group consisting of aluminum nitride, boron nitride, silicon nitride, and mixtures thereof,
- (b) between about 10 and about 45 vol % of a semiconductive material selected from the group consisting of silicon carbide and boron carbide, and mixtures thereof, and
- (c) between about 8.5 and about 14 vol % of a metallic conductor selected from the group consisting of molybdenum disilicide, tungsten disilicide, tungsten carbide, titanium nitride, and mixtures thereof.

In more preferred embodiments, the hot zone comprises a first resistive material comprising between 50 vol % and 75 vol % AlN, between 13 vol % and 41.5 vol % SiC, and between 8.5 vol % and 12 vol % MoSi₂. In other embodiments, the hot zone further comprises between 1 v/o and 10 v/o alumina, preferably in accordance with U.S. Pat. No. 5,514,630, the specification of which is incorporated by reference herein.

Referring now to FIG. 3, the hot zone typically has a thickness T_{hz} of between about 0.05 cm and 0.2 cm, preferably between about 0.06 cm and 0.125 cm. Its length L_{hz} (which, in FIG. 3, is the same as the electrical path length) is generally between 0.05 cm and 0.45 cm, preferably between 0.15 cm and 0.25 cm. Its depth D_{hz} is generally between 0.05 cm and 0.4 cm, preferably between 0.1 cm and 0.25 cm.

Preferably, the particle sizes of both the starting powders and the grains in the densified hot zone are similar to those described in the '804 patent. In some embodiments, the average grain size (d_{50}) of the hot zone components in the densified body is as follows: a) electrically insulative material (i.e., AlN): between about 2 and 10 microns; b) semiconductive material (i.e., SiC): between about 1 and 10 microns; c) and metallic conductor (i.e., MoSi₂): between about 1 and 10 microns.

In some embodiments, the hot zone comprises a pair of resistive sections disposed in parallel between the conductive ends. For example, as shown in FIG. 4, the hot zone can comprise first resistive section 15 and second resistive section 17, each of which is in parallel electrical connection with each of the conductive ends 9 and 13. In this particular embodiment, the first section is designed to have a lower resistivity than the second section. Without wishing to be tied to theory, it is believed that, at room temperature, the first resistive section has a sufficiently low resistivity to provide the speed needed to heat the igniter, while the second section has a sufficiently high resistivity to inhibit the inrush current. At high temperatures (i.e., 1350° C.), it is believed the relatively high resistivity of the second resistive section is sufficiently high (relative to the first resistive section) so as to prevent overpowering of the igniter.

Preferably, second resistive section 17 of the hot zone has the same thickness and length as the first resistive section. Its depth is generally between about 0.25 cm and about 0.125 cm, preferably between 0.05 cm and 0.1 cm. Its room temperature resistivity and its 1350° C. resistivity are typically higher than those corresponding to the first resistive section.

In one embodiment of the invention, the second resistive section is formed in-situ by a reaction between the powders

selected to form the first resistive section 15 and powders selected to form electrically insulating heat sink 19 disposed between the legs of a conventional hairpin igniter. Without wishing to be tied to a theory, it is believed that the conductive components of the first resistive section 15 preferentially diffuse into the powders of the electrically insulating heat sink 19 and react therewith, thereby creating a diffuse second resistive section 17 typically having a depth of between about 1% to about 20% of the depth of the first resistive section 15.

The function of the electrically insulating heat sink material 19 is to provide sufficient thermal mass to mitigate convective cooling of the hot zone. When disposed as an insert between the two conductive legs, it also provides mechanical support for the conductive legs 9 and 13 and so makes the igniter more rugged. The insert typically has a thickness and length similar to conductive legs 9 and 13 and a width equal to the portion of the hot zone which bridges the legs. In some embodiments, the insert may be provided with a slot 40 (as in FIG. 3) to reduce the mass of the system. Preferably, the electrically insulating heat sink has a resistivity of at least about 10^4 ohm-cm and a strength of at least about 150 MPa. More preferably, the heat sink material has a thermal conductivity which is not so high as to heat the entire heat sink and transfer heat to the leads, and not so low as to negate its beneficial heat sink function. Suitable ceramic compositions for the heat sink include compositions comprising at least 90 v/o of (and preferably consisting essentially of) at least one of aluminum nitride, boron nitride, silicon nitride, alumina, and mixtures thereof. In embodiments using an AlN—MoSi₂—SiC hot zone, it was found that a heat sink material comprising at least 90 vol % aluminum nitride and up to 10 vol % alumina possessed compatible thermal expansion and densification characteristics. However, it was found that the alumina also inhibited the reaction needed for the effective formation of the in-situ second resistive section. Accordingly, when in-situ formation of the second resistive section is contemplated, the insert preferably consists essentially of at least one of aluminum nitride, boron nitride, and silicon nitride, and mixtures thereof, more preferably aluminum nitride. Likewise, when the hot zone is designed to have a less significant in-situ formed resistive section, the electrically insulating heat sink material comprises between 1 v/o and 10 v/o alumina. In other embodiments, 1–10 v/o of the insert is a densification aid selected from the group comprising alumina, calcia, magnesia, silica and (preferably) yttria, and mixtures thereof. In preferred embodiments, the dimensions of the inserts are 4.0 cm (depth)×0.25 cm (width)×0.1 cm (thickness).

Conductive ends 9 and 13 provide means for electrical connection to wire leads. Preferably, they also are comprised of AlN, SiC and MoSi₂, but have a significantly higher percentage of the conductive and semiconductive materials (i.e., SiC and MoSi₂) than do the preferred hot zone compositions. Accordingly, they typically have much less resistivity than the hot zone and do not heat up to the temperatures experienced by the hot zone. They preferably comprise about 20 to 65 v/o aluminum nitride, and about 20 to 70 v/o MoSi₂ and SiC in a volume ratio of from about 1:1 to about 1:3. More preferably, the conductive ends comprise about 60 v/o AlN, 20 v/o SiC and 20 v/o MoSi₂. In preferred embodiments, the dimensions of conductive ends 9 and 13 are 0.05 cm (width)×4.2 cm (depth)×0.1 cm (thickness). In other embodiments, conductive metal can be deposited upon the heat sink material and hot zone to form the conductive legs.

Also in accordance with the present invention, there is provided a preferred method of making the present invention, wherein tiles made of warm pressed powder mixtures having predetermined compositions are arranged so that the tile cross-section depicts an electrical circuit. In one preferred process for making the invention (and as shown in FIG. 5), a first tile 21 consisting essentially of a conductive portion is laid on a flat surface (not shown). A second tile 24 having an insulative portion 26 and a first resistive material 28 is then laid atop the first tile 21 in the manner shown. Next, a third tile 32 having only a conductive section is laid atop the second tile. This laminate is then densified so that the disparate tiles join. The densified laminate is then sliced across its thickness to form a plurality of individual ceramic igniters.

In making the present invention, each green tile shown in FIG. 5 comprises an entire layer of the ceramic laminate (e.g., second tile 24 has an insulative portion 26 and resistive section 28). Alternatively, the tiles may consist of only one portion of a layer. In the latter case, it has been found that tiles comprising a portion of a layer may be glued together without any attendant loss in properties.

Although FIG. 5 presents each layer as rigid green tiles, these portions alternatively can be made by either tape casting, roll compaction, warm pressing followed by slicing, dry pressing or screen printing. In another preferred embodiment, as shown in FIG. 6, green tape 60 having a conductive composition is wrapped around three sides of a tile having an electrically insulating heat sink 61 and a hot zone 62. After densification, a portion of the tape which wraps around the hot zone is removed by grinding, as shown by the dotted line A in FIG. 6, to provide the desired circuit. Optionally, the igniter can be further ground along dotted line B to produce a rounded tip, match stick appearance.

When the igniter uses the electrically insulating heat sink material as an insert, the igniter may be made by the general method disclosed in U.S. Pat. No. 5,191,508, the specification of which is incorporated by reference.

The processing of the ceramic component (i.e., green body processing and sintering conditions) and the preparation of the igniter from the densified ceramic can be done by any conventional method. Typically, such methods are carried out in substantial accordance with the '804 patent, the specification of which is incorporated by reference. In preferred embodiments, the green laminates are densified by hot isostatic pressing in a glass media as disclosed in U.S. Pat. No. 5,514,630, the specification of which is incorporated by reference. The densification yields a ceramic body whose hot zone has a density of at least 95%, preferably at least about 99%, of theoretical density. The average grain size of the densified hot zone is typically between 1 and 10 μ m, preferably between 1 and 3 μ m.

The igniters of the present invention may be used in many applications, including gas phase fuel ignition applications such as furnaces and cooking appliances, baseboard heaters, gas or oil boilers and stove tops. In one preferred embodiment, four 30 V igniters of the present invention are provided in series and used as ignition sources for gas-fired heating elements on a 120 V gas range.

Although the igniter of the present invention is typically used in the voltage range of 3V to 60 V, it is more typically used in the range of 12V to 40V. In the 3–9V range, it is believed that using a smaller hot zone length and/or increasing the MoSi₂ content would provide the lower resistance needed to produce suitable properties.

In addition, the exposed resistive hot zones of the present invention display a higher surface loading of power, mea-

sured in watts/cm² of the hot zone surface area, than the conventional '804 style igniter. The exposed resistive hot zone surface loading of the igniters of the present invention, which is typically between 200 and 400 watts/cm², represents an improvement over the '804-style igniter, which could provide a surface loading of only about 20-40 watts/cm² (see Table at col. 7-8 of the '804 patent) before experiencing burnout. Without wishing to be tied to a theory, it is believed the higher surface loading is the reason why the igniters of the present invention are much more resistant to convective cooling.

In some embodiments, the hot zone and/or the legs can be coated with a layer of a protective ceramic such as CVD AlN or Si₃N₄. In these embodiments, the coated igniter is protected from carbon and soot depositing on the small hot zone and causing a short.

The practice of the present invention can be further appreciated from the following non-limiting Examples and Comparative Examples. For the purposes of the present invention, a "stable" igniter is one which maintains a constant resistivity and a constant temperature at a given voltage.

EXAMPLE I

A green laminate was constructed in substantial accordance with the design shown in FIG. 5. A composite powder comprising a hot zone powder mixture of 64 v/o AlN, 25 v/o SiC, and 11 v/o MoSi₂, next to an electrically insulating heat sink powder consisting essentially of 100 v/o aluminum nitride powder was warm pressed to form a billet which was then sliced to form green tile 24 of FIG. 5. The hot zone portion of the warm pressed green body had a density of about 63% of theoretical density, while the AlN portion had a density of about 60% of theoretical density. The green tiles representing the conductive ends were made by warm pressing powder mixtures containing 20 v/o AlN, 60 v/o SiC, and 20 v/o MoSi₂ to form a billet having a density of about 63% of theoretical density, from which tiles 21 and 32 of FIG. 5 were sliced. The green tiles were laminated as in FIG. 5, and then densified by glass hot isostatic pressing at about 1800° C. for about 1 hour to form a ceramic block having an in-situ formed second resistive section. The block was then sliced across its width to produce a plurality of hot surface elements measuring 1.5"x0.150"x0.030" (3.81 cm×0.75 cm×0.076 cm). The resulting hot zone comprised a first resistive section having a depth of about 0.125 cm, and an in-situ formed second resistive section having a depth of about 0.05 cm. The hot zone length (EPL) and thickness were about 0.25 cm and 0.076 cm, respectively.

Suitable leads were attached to the conductive portions of the hot surface element and a voltage of about 30 V was applied.

The electrical performance of the resulting nominal 24V igniter is shown in FIG. 7 in terms of voltage and temperature. Since the low temperature resistance is lower than the high temperature resistance, the hot zone has an effective PTCR. The igniter displayed stable heating performance and reached the design temperature of 1100° C.-1350° C. in only about 1.0 second. As shown in FIG. 8a, the inrush current was found to be only 3.2 amperes. The power, which was measured at 54 watts, provided an exposed resistive hot zone surface loading of about 300 watts/cm².

EXAMPLE II

This example is intended to show the superior resistance to convective cooling provided by the igniter of the present invention as compared to those in Comparative Example I below.

An igniter was made in substantial accordance with Example I. The electrical path length of this igniter was 0.25 cm. When this igniter was energized with 24V, it produced a current of 1.8 amps and a stable temperature of 1408° C.

A gas canister which provides 400 cc/min (ccm) of air was placed about 1 foot from the igniter. A stream from the air jet only reduced the hot zone temperature to about 1182° C. The air jet did not blow out the igniter.

Comparative Example I

A conventional 24V igniter marketed by the Norton Company under the '804 patent was selected for comparison. It had an hot zone electrical path length of about 2.05 cm. When energized with 24V, it reached about 1100° C.-1350° C. in about 2-3 seconds, and produced at stable temperature of 1410° C. As shown in FIG. 8b, it had an in-rush amperage of about 11 amps which settled down to about 3 amps. A stream from the air jet described above reduced the hot zone temperature to about 950° C., which is below the desired 1100° C. minimum.

A conventional 12V igniter marketed by the Norton Company under the '804 patent was energized with 12V and produced a stable current of about 2.0 amps and a stable temperature of 1400° C. A stream from the air jet described above reduced the hot zone temperature to less than 600° C.

EXAMPLE III

This example shows the superior life testing results of the igniter of the present invention.

A 24 V igniter similar to that used in Example II was subjected to life cycle testing, wherein the igniter is turned on for 20 seconds and then turned off for 20 seconds. After 543,000 cycles, the decrease in amperage was only 5.43%. This small change represents an improvement over the standard '804 patent igniter, which typically showed a 16% decrease over similar cycling. The temperature of the igniter of the present invention was originally was about 1393° C. and only decreased to about 1379° C. over the life cycle test.

EXAMPLE IV

This example examines the behavior of an igniter wherein the hot zone composition is contacted by an electrically insulating heat sink material whose composition inhibits formation of an in-situ formed resistive section. In particular, it shows the benefit provided by the in-situ formed second resistive portion in decreasing in-rush amperage.

An igniter was made in a substantially similar manner to the igniter described in Example II above, except that 4 v/o alumina was added to the insert composition to inhibit in-situ formation of a second resistive composition.

Examination of the microstructure of the resulting ceramic revealed a lesser degree of in-situ formation of a second resistive section. It is believed the alumina addition effectively inhibited the formation of a second resistive section.

When a 24V voltage was applied to this igniter, it reached about 1350° C. in about 1 second and was stable. As shown in FIG. 8c, its in-rush amperage was only 4 amps, and so was lower than the inrush amperage of the conventional '804-style igniter but higher than that of Example I. It later settled to about 2 amps.

Comparative Example II

This comparative example demonstrates the superior surface loading of the igniter of the present invention.

A standard 24V igniter was energized with 24V and produced a stable temperature and a 1.57 amperage. When the voltage was increased to 35 volts (thereby producing an amperage of 2.3 amps), the igniter failed. The surface loading of the igniter at failure was only about 60 watts/cm². By comparison, the igniter of Example I had an exposed resistive hot zone surface loading of about 300 watts/cm².

We claim:

1. A ceramic igniter comprising:

- a) a pair of electrically conductive portions, each portion having a first end.
- b) a resistive hot zone disposed between and in electrical connection with each of the first ends of the electrically conductive portions, the hot zone having an electrical path length of less than 0.5 cm. and
- c) an electrically non-conductive heat sink material contacting the hot zone.

2. The igniter of claim 1 wherein the hot zone has a room temperature resistivity of between about 0.01 ohm-cm and about 3.0 ohm-cm and a 1350° C. resistivity of between about 0.001 ohm-cm and about 3.0 ohm-cm.

3. The igniter of claim 1 wherein the hot zone comprises a first resistive material having a composition comprising:

- (a) between about 50 and about 75 vol % of an electrically insulating material selected from the group consisting of aluminum nitride, boron nitride, silicon nitride, and mixtures thereof.
- (b) between about 10 and about 45 vol % of a semiconductive material selected from the group consisting of silicon carbide and boron carbide, and mixtures thereof, and
- (c) between about 8.5 and about 14 vol % of a metallic conductor selected from the group consisting of molybdenum disilicide, tungsten disilicide, tungsten carbide, titanium nitride, and mixtures thereof.

4. The igniter of claim 3 wherein the electrically non-conductive heat sink material is a ceramic selected from the group consisting of AlN, Si₃N₄, BN, Al₂O₃, and mixtures thereof.

5. The igniter of claim 3 wherein the electrically conductive portions further comprise second ends extending in the same direction from the hot zone to define a pair of legs, and the electrically non-conductive heat sink material is disposed between the legs.

6. The igniter of claim 3 wherein the hot zone further comprises an in-situ formed resistive portion disposed between the first resistive material and the electrically non-conductive heat sink material.

7. The igniter of claim 3 wherein the hot zone further comprises a second resistive material having a resistivity which is higher than the resistivity of the first resistive material.

8. The igniter of claim 3 wherein the electrically non-conductive heat sink material comprises at least 90 v/o of a ceramic selected from the group consisting of AlN, Si₃N₄, BN, Al₂O₃, and mixtures thereof.

9. The igniter of claim 8 wherein the electrically non-conductive heat sink material consists essentially of AlN.

10. The igniter of claim 3 wherein the hot zone further comprises between 1 and 10 v/o Al₂O₃.

11. The igniter of claim 3 where the first resistive material comprises between 50 vol % and 75 vol % AlN, between 12 vol % and 41.5 vol % SiC, and between 8.5 vol % and 12 vol % MoSi₂.

12. The igniter of claim 3 wherein the hot zone has an electrical path length of between 0.05 and 0.45 cm.

13. The igniter of claim 3 wherein the hot zone has an electrical path length of between 0.15 cm and 0.25 cm.

14. The igniter of claim 3 wherein the hot zone has a thickness of between 0.05 cm and 0.2 cm, and a depth of between 0.05 cm and 0.4 cm.

15. The igniter of claim 3 wherein the hot zone has an average grain size of between 1 and 10 μ m.

16. The igniter of claim 3 wherein the hot zone has an average grain size of between 1 and 3 μ m.

17. The igniter of claim 3 wherein the hot zone has a density of at least 95% of theoretical density.

18. The igniter of claim 3 wherein the hot zone has a density of at least 99% of theoretical density.

19. The igniter of claim 7 wherein the second resistive material has a depth of between about 1% and about 20% of the depth of the first resistive material.

20. The igniter of claim 8 wherein the electrically insulating heat sink material further comprises a sintering aid selected from the group consisting of yttria, magnesia, calcia and silica, and mixtures thereof.

21. A method of heating, comprising the steps of:

a) providing a ceramic igniter comprising:

- i) a pair of electrically conductive portions, each portion having a first end,
- ii) a resistive hot zone disposed between and in electrical connection with each of the first ends of the electrically conductive portions, the hot zone having an electrical path length of less than 0.5 cm, and
- iii) an electrically non-conductive heat sink material contacting the hot zone.

b) applying a voltage of between 3 V and 60 V between the conductive ends of the igniter to produce an inrush current and a steady state current such that the ratio of the steady state current to the inrush current is at least 35%, and raising the temperature of the hot zone to about 1350° C. in less than about 3 seconds.

22. The method of claim 21, wherein the ratio of the steady state current to the inrush current is at least 50%.

23. The method of claim 21 wherein the resistive hot zone comprises a first resistive material having a composition comprising:

(a) between about 50 and about 75 vol % of an electrically insulating material selected from the group consisting of aluminum nitride, boron nitride, silicon nitride, and mixtures thereof.

(b) between about 10 and about 45 vol % of a semiconductive material selected from the group consisting of silicon carbide and boron carbide, and mixtures thereof, and

(c) between about 8.5 and about 14 vol % of a metallic conductor selected from the group consisting of molybdenum disilicide, tungsten disilicide, tungsten carbide, titanium nitride, and mixtures thereof.

24. The method of claim 21 wherein the resistive hot zone comprises a first resistive material comprising between 50 vol % and 75 vol % AlN, between 13 vol % and 41.5 vol % SiC, and between 8.5 vol % and 12 vol % MoSi₂.

United States Patent [19]

Washburn

[11] Patent Number: 5,045,237

[45] Date of Patent: Sep. 3, 1991

[54] REFRACTORY ELECTRICAL DEVICE

[75] Inventor: Malcolm E. Washburn, Princeton, Mass.

[73] Assignee: Norton Company, Worcester, Mass.

[21] Appl. No.: 258,307

[22] Filed: Oct. 14, 1988

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 120,291, Nov. 13, 1987, abandoned, which is a continuation-in-part of Ser. No. 669,399, Nov. 8, 1984, abandoned.

[51] Int. Cl.⁵ H01B 1/18

[52] U.S. Cl. 252/516; 252/518; 501/89; 501/92; 501/98; 219/270; 219/553

[58] Field of Search 501/88, 89, 92, 96, 501/98, 97; 252/516, 518, 548; 219/553, 270

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3,246,275 4/1966 Schrewelius 501/92
3,252,827 5/1966 Rose et al. 117/201
3,649,310 3/1972 Yates 501/89
3,813,252 5/1974 Lipp 252/520
3,875,476 4/1975 Crandall et al. 317/98
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3,890,250 6/1975 Richerson 252/516

3,926,857 12/1975 Matkin et al. 501/92
3,974,106 8/1976 Richerson 252/516
4,120,827 10/1978 Boos et al. 501/88
4,174,971 11/1979 Schrewelius 106/44
4,184,882 1/1980 Lange 501/92
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1058673 7/1979 Canada 309/96
0027653 2/1985 Japan 501/89
0936118 9/1963 United Kingdom 501/92

Primary Examiner—Karl Group

Attorney, Agent, or Firm—Arthur A. Loiselle, Jr.

[57] ABSTRACT

The present invention is an electrical device made up of a mixture of silicon carbide and molybdenum disilicide, and may include silicon nitride or aluminum nitride or boron nitride. An electrical device is also disclosed which is particularly suited for use as an igniter in liquid and gas fuel burning systems. The device is made up of a sintered, preferably hot-pressed, mixture of fine powders of aluminum nitride or silicon nitride, silicon carbide and molybdenum disilicide where, when all three are present, they are present in substantial quantities.

10 Claims, 2 Drawing Sheets

1/2

FIG. 1

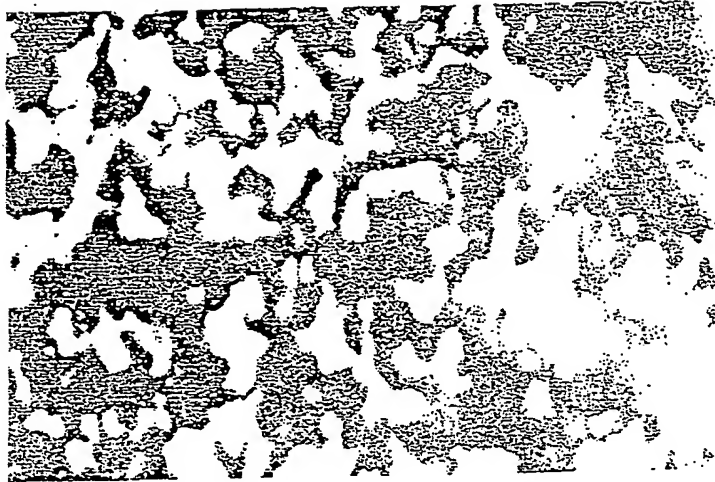


FIG. 2

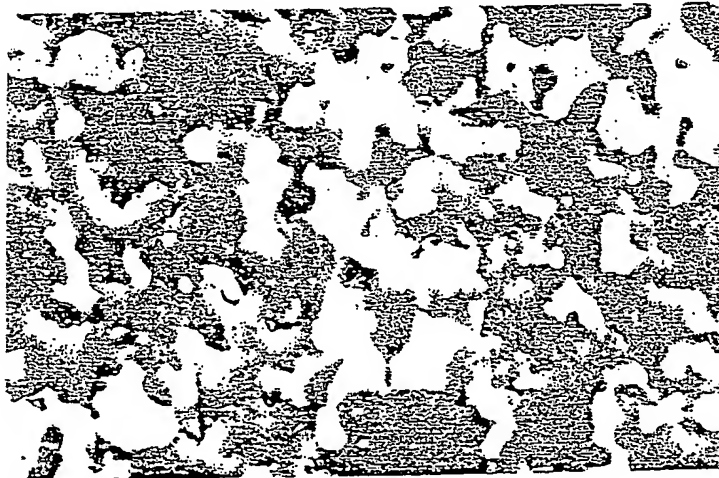
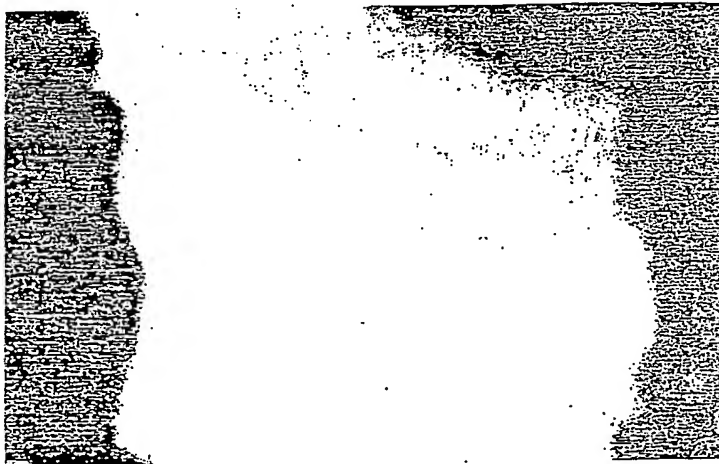


FIG. 3



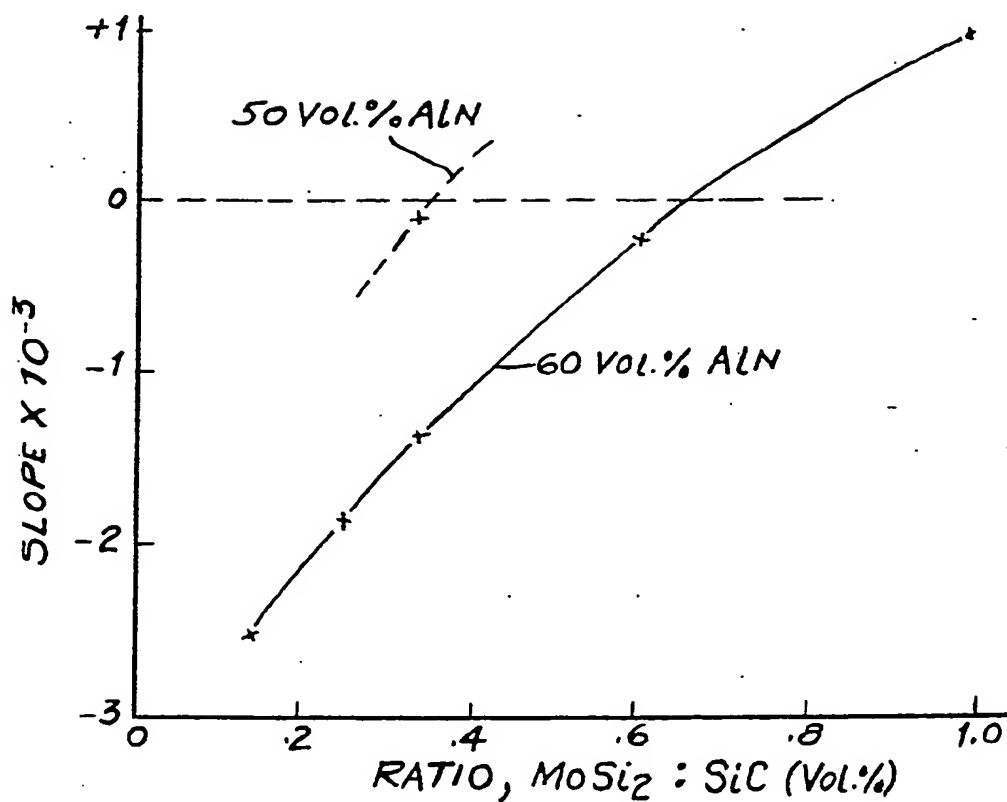


FIG. 4

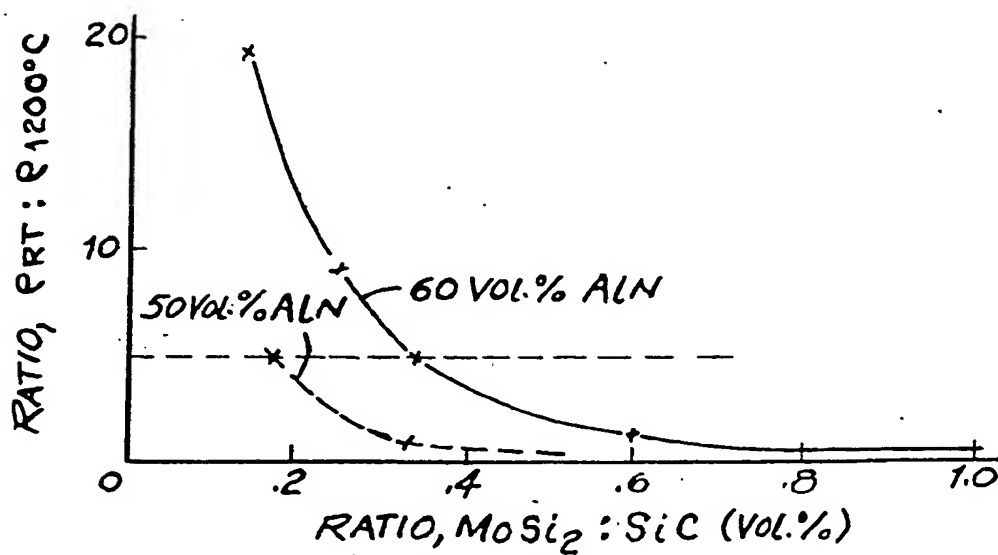


FIG. 5

REFRACTORY ELECTRICAL DEVICE

This is a continuation-in-part application of application Ser. No. 07/120,291 filed Nov. 13, 1987 and, which in turn is a continuation-in-part of application Ser. No. 06/669,399 filed Nov. 8, 1984, now abandoned.

TECHNICAL FIELD

The invention is concerned with ceramic or refractory electrical devices and their particular utility as heating elements, igniters, and heat sensors.

BACKGROUND AND INFORMATION
DISCLOSURE STATEMENT

The following patent publications are representative of the most relevant prior art known to the Applicant at the time of filing of the application.

U.S. PATS.		
3,252,827	May 24, 1966	C. G. Rose et al
3,649,310	March 14, 1972	P. C. Yates
3,813,252	May 28, 1974	A. Lipp
3,875,476	April 1, 1975	W. B. Crandall et al
3,875,477	April 1, 1975	J. I. Fredriksson et al
3,890,250	June 17, 1975	D. W. Richerson
4,174,971	November 20, 1979	N. G. Schrevelius
4,205,363	May 27, 1980	C. J. Boos et al
FOREIGN PATENTS		
1,058,673	July 17, 1979	Canada

The utility of ceramic or refractory compositions for electrical devices such as resistors has been known for many years. Silicon carbide heating elements have found widespread use. In more recent years, primarily as a result of the so-called energy crunch, attention has been focused on the application of ceramic resistors as igniters in, for example, gas fired furnaces and appliances like stoves and clothes driers. An example of such an igniter is taught in U.S. Pat. No. 3,875,477. The igniter is mainly composed of 95 to 99.9% by weight of silicon carbide and 0.05 to 0.50% by weight of aluminum, with optional minor quantities of silica and iron. The terminal connecting ends, or so-called cold ends, are formed in the conventional manner by metal coating said ends by dipping in a molten metal or flame spraying. These igniters are relatively low density bodies as a result of the process used to fabricate them viz. slip casting. Therefore they are susceptible to degradation.

An earlier approach to protecting very porous (35% by volume) silicon carbide type heating elements from oxidative degradation is that taught by U.S. Pat. No. 3,252,827. This is accomplished by first forming a porous self-bonded silicon carbide rod which is then immersed in an aqueous suspension of finely divided molybdenum disilicide for a sufficient amount of time to allow the molybdenum disilicide particles to fully penetrate the silicon carbide body and coat the walls of the pores contained therein. The body is then fired in an inert atmosphere to sinter the silicide to form the final coating. Ten to twenty five percent molybdenum disilicide can be used. While this approach is effective for a relatively large body such as a heating element e.g. having a diameter of 0.5 inch (1.27 cm) or larger, they are porous and therefore relatively mechanically weak. Therefore the teachings of this patent would not produce a commercially acceptable product where the product must have a small cross section of, for example, an igniter such as that of U.S. Pat. No. 3,875,477 with a

cross sectional area of from 0.012 to 0.072 in² (0.77×10^{-3} to 0.46×10^{-2} cm²). The composition of U.S. Pat. No. 3,252,827 would result in an igniter that would simply be too fragile for practical use.

U.S. Pat. No. 4,174,971 offers a solution to the problem of relatively weak heating elements and the like. This reference impregnates a silicon carbide body with what is referred to as a molybdenum-silicon alloy which finally ends up as 25% of the structure; the impregnant is made up of about 50% by weight of silicon and 50% by weight of molybdenum disilicide.

High strength refractory resistor compositions are taught by U.S. Pat. No. 3,890,250. The product is composed of from 50 to 90% by weight of silicon nitride and 10 to 50% by weight of silicon carbide and has a modulus of rupture in excess of 100,000 psi (689 MPa) at 20° C. as measured by four point loading. The electrical resistivity varies from 1 to 1×10^7 ohm cm. These high strength characteristics are the result of hot-pressing the mixture of powders which brings about almost complete densification. However, when this material is used as an igniter the hot zone degrades rather quickly e.g. goes from a resistance of 182.4 to 247.4 ohms after only 311 hours at 1200° C. and the cold ends or tabs from 40.4 ohms to 154.4 ohms.

A dense submicron grained silicon carbide-aluminum nitride body is disclosed by U.S. Pat. No. 3,649,310 which is suitable for use as a heating element, amongst other things. The composition may also contain up to 80% of boron carbide, alumina and silicon nitride. The product is made by hot-pressing a mixture of submicron sized aluminum carbide and silicon nitride at about 2000° C. The two materials react with each other to form a mixture of submicron particles of aluminum nitride and silicon carbide. The resulting material has a density close or equal to theoretical density.

U.S. Pat. No. 3,875,476 specifically teaches a heat resistant ceramic electrical igniter which is composed principally (25-88%) of silicon carbide and a pyrex glass bond (5-30%); the composition may also include 1-8% ferro-silicon, 1-10% titania, 1-20% zirconia, and 5-30% silica. While not discussed in detail and not included as an example, the reference states that there are other possible mixtures of components including some containing molybdenum disilicide MoSi₂. In order to keep the terminal ends cool, the igniter of this patent has a composition, based on the above compounds, which varies from one with a relative high resistance in the center or hot-zone to one with substantially lesser resistance in the terminal ends. To avoid problems resulting from significantly different coefficients of thermal expansion, the reference employs several compositions going from the hot-zone to the terminal ends so that there is a gradual compositional transition and a resulting gradual transition in the coefficient of thermal expansion of the various portions of the igniter. This eliminates premature cracking of the igniter as a result of dramatically different thermal expansion characteristics. While the reference does not limit the configuration of the igniter, i.e. apparently the igniter may take any known shape, what is shown is a U-shaped device with the ends of the legs of the U being the terminal connector ends. The shape could of course be straight or more complexly configured as shown in Canadian Patent No. 1,058,673 and U.S. Pat. No. 3,875,477.

A complex refractory composition is the subject of U.S. Pat. No. 3,813,252. The sintered refractory mate-

rial is made up of 10-20% of boron nitride with 20-80% of the remainder being selected from the group consisting of aluminum nitride, aluminum boride and silicon nitride, and 20-80% of that remainder being selected from the group consisting of graphite, boron carbide, titanium carbide, zirconium carbide, chromium carbide, silicon boride, beryllium boride, magnesium boride and calcium boride. The closest this teaching comes to the present invention is a mixture of boron nitride, aluminum nitride (or silicon nitride) and silicon carbide. What is missing is the all important molybdenum disilicide.

Another igniter for stove top burners which utilize gas is that described by U.S. Pat. No. 4,205,363. The igniter is composed essentially of silicon carbide, i.e. at least 95% silicon carbide and up to 5% of a negative doping agent in the form of such elements as nitrogen, phosphorus, arsenic, antimony and bismuth. The igniter can have a ratio of room temperature resistivity to resistivity at 1200° C. of less than 12 to 1 and preferably less than 9 to 1. By contrast, the present invention igniter can be formulated to have such a ratio as high as 19.8 but more importantly as low as 0.2. Heat up time, as is well known, is critical to the successful and safe use of a resistance igniter for the purpose of igniting gas. The reference discloses response times, i.e. time for the igniter to reach about 1250° C. from room temperature, in 2 or 3 seconds. To accomplish this rapid response time the igniter must be made very small in cross-section, more specifically, a cross section of 0.0002 to about 0.004 square centimeters. Thus the resulting igniter is essentially a silicon carbide hair or filament which is in turn extremely fragile. The invention igniter does not possess that shortcoming.

Lastly, Canadian Patent No. 1,058,673 discloses a complexly shaped igniter element wherein the hot-zone is made up essentially of recrystallized silicon carbide and the hot-zone includes a continuous groove therein. The silicon carbide contains an electrical resistivity modifying agent such as aluminum oxide, molybdenum disilicide, magnesium fluoride, magnesium chloride or magnesium titanate or a combination of these compounds. The quantity of electrical resistivity modifier to be added, according to the patent is about 10% by weight although as much as 25% alumina in the silicon carbide is taught. Silicon nitride is also mentioned as another electrical resistivity modifying agent usable to change the resistance of the shape and to impart desirable physical properties to the igniter.

The principal differences between the present invention and the prior art are the superiority of the invention resistor, particularly when utilized as an igniter, and the novel composition thereof which is what produces the superior results.

DISCLOSURE OF THE INVENTION

The total structure developed in the refractory body of the invention is essentially that of 2 separate but intertwined structures with one structure being contained within the other structure. FIGS. 1 and 2 are SEM's taken at 2000X of polished sections of two different mixtures showing similar structures of a dark gray continuous phase and a light gray continuous phase, with continuities being made 3 dimensionally. The dark gray structure is a dense nitride that is strong and rigid with connecting paths up to about 10 microns in width. The light gray structure is a dense continuous structure that because of its softer nature at elevated

temperature has flowed into the interstices of the rigid structure.

FIG. 1 shows an example of a 50 volume % aluminum nitride rigid structure with a 50 volume % MoSi₂ and SiC electrically conductive structure with 30 volume % MoSi₂ and 20 volume % SiC. FIG. 2 shows a 60 volume % AlN rigid structure with 40 volume % of the mixture of MoSi₂ and SiC where the MoSi₂ is 15 volume % and the SiC is 25 volume %.

X-ray diffraction patterns show three distinct and well defined phases of AlN, MoSi₂ and SiC with no additional phases. The light gray phase is seen in FIG. 3 as an SEM taken at 17000X and shows sharp definition between the dark SiC and AlN structure and the light grey MoSi₂. While the preferred compositions incorporate silicon carbide, molybdenum disilicide and a nitride, compositions of from 5% to 50% by volume of molybdenum disilicide and 50% to 95% by volume of silicon carbide are also within the concept of the present invention.

It is believed that an essential feature of this type of total structure is that even though there is intimate contact between the two intertwined structures there is no or very little chemical reaction between or diffusion of cations from one structure to the other. This has been shown by EDAX analysis in the AlN; MoSi₂ and SiC system. Because of this, each structure can contribute its distinctive properties to the total system without interference of an undesired phase between the two structures. In this way the total system can have special characteristics because of interplay of properties. An example would be to select structures with different thermal expansions in which the metallic structure would put the brittle structure into compression for increased toughness of the total system. Another example would be a relatively softer metallic structure to act as an energy absorber for improved impact resistance. Another example would be for a strong high temperature resistant structure to act as a reinforcement for a structure that would be weak or soft at high temperature. Another important example would be as a strong high temperature electrically, non conductive structure to act as a reinforcement for an electrically conductive structure that can be varied in its electrical characteristics as desired.

The strong rigid structure may be made from nitrides such as Si₃N₄, AlN, or combinations. In the case of Si₃N₄, a sintering aid would be required to achieve high density but no sintering aid would be necessary for AlN.

The electrically conductive structure may have varying ratios of MoSi₂ and SiC to vary both the magnitude and the nature of the conductivity. For example, ratios that are high in MoSi₂ are low in resistivity and ratios that are low in MoSi₂ are high in resistivity. When the ratio of MoSi₂ to SiC is higher than 0.65 in a composition containing 60 volume % AlN, the resistivity at elevated temperatures is higher than the resistivity at room temperature. The slope of the resistivity curve with temperature is positive similar to that of metallic conduction. When the ratio is less than 0.65 in the 60 volume % AlN composition, the resistivity curve has a negative slope similar to that of a semiconductor such as SiC. When the ratio equals 0.65, the slope is zero and the hot resistivity is equal to the cold resistivity. Table I shows summarized data of electrical igniters made from various mixtures of AlN, MoSi₂ and SiC.

FIG. 4 shows the relationship of the slope of the resistivity curve, and the ratio of MoSi₂ to SiC for a semilog curve with the equation as shown. With a composition based on 50 volume % AlN instead of 60 volume %, the ratio of MoSi₂ to SiC is 0.33 when the slope is equal to zero.

A main feature of the embodiment of this invention which is an electrical igniter for fluid fuels i.e. gas and liquid fuels, is that both the magnitude of resistivity and the slope of the resistivity curve may be controlled by varying the two structures with these three ingredients. Increases in the nitride structure will result in increases in the magnitude of the resistivity and vice versa. Increases in the ratio of MoSi₂ and SiC in the conductive structure will result in decreases in the ratio of cold resistivity to hot resistivity. These decreases in turn, result in decreases in the response time of the igniter.

FIG. 5 shows the relationship of the ratio of cold resistivity to hot resistivity with the ratio of MoSi₂ to SiC. In a composition with 60 volume % AlN, resistivity ratios of 5 or less would be at MoSi₂:SiC ratios of 0.33 or greater. Similarly in a composition with 50 volume % AlN for a resistivity of 5 or less the MoSi₂:SiC would be 1.8 or greater.

TABLE I

	Example #						
	III	IV	V	VI	VII	VIII	IX
AlN, Vol %	60	60	60	50	60	60	50
MoSi ₂ , #	5	7.9	10	12.5	15	20	30
SiC, #	35	32.5	30	37.5	25	20	20
Density, % Theor.	96.1	92.9	95.9	96.1	95.5	91.1	99.0
Resistivity: 52 cm (R) Measured.							
30°	89.8	70	5.22	.27	.33	.0029	.0006
1200°	12.8	—	1.03	.24	.12	.019	.0035
Calculated.							
30°	214	27.2	6.12	—	.18	.0050	—
1200°	10.8	3.06	1.23	—	.14	.016	—
Ratio, R ₃₀ :R ₁₂₀₀	19.8	8.9	5.0	1.1	1.3	.3	.2
Slope*** (× 10 ⁻³)	-2.55	-1.87	-1.37	-1.0	-2.1	+99	+1.5
Ratio, MoSi ₂ :SiC	.143	.246	.333	.333	.60	1.0	1.5

*R₃₀ = 7457.3 · E (-7105 · M) correlation coefficient = .984

**R₁₂₀₀ = 94.244 · E (-4338 · M) correlation coefficient = .997

***R_T = A · E (B · T)

SemiLog curves where:

R = Resistivity

M = Vol % MoSi₂

T = Temperature

E = Natural logarithm

A = Intercept

B = Slope

The major disadvantages possessed by prior art ceramic electrical resistors, particularly igniters, are the tendency to oxidize and degrade in use causing the resistivity to increase unacceptably, and an inherently high ratio of room temperature resistivity to resistivity of elevated temperature e.g. 1200° C. which requires a high energy input to get the resistor up to the desired temperature. The ceramic igniter taught by U.S. Pat. No. 4,120,827 suffers from both of the foregoing shortcomings. Because it is composed of essentially only silicon carbide, it oxidizes. The patented igniter in some cases has a ratio of room temperature to elevated temperature resistivities of 5.5 which is good relative to other prior art devices but is still undesirably high in applications requiring a rapid response time i.e. heating time from room temperature to 1200° C.

It has now been found that the deficiencies of the prior art are greatly minimized by utilizing the composition of the present invention. Electrical igniters with ratios of room temperature resistivity to resistivity at

1200° C. as low as 0.2 result from a sintered or hot-pressed volume percent mixture of from 30% to 70% of a nitride of aluminum, silicon, or boron; 10% to 45% of silicon carbide; 5% to 50% of molybdenum disilicide; and 0 to 3% of a sintering aid such as a source of magnesium oxide; which has been hot-pressed or sintered to a density of at least 85% of theoretical density. Thus the operable ranges of the materials making up the present invention are 5 to 50% by volume of molybdenum disilicide and 50 to 95% by volume of a material selected from the group consisting of silicon carbide, silicon nitride, aluminum nitride, boron nitride, aluminum oxide, magnesium aluminate, silicon aluminum oxynitride, and mixtures thereof. The most preferred igniter contains 4% or less of open porosity. Sintering or pressing aids such as magnesium carbonate are well known and while the use of such a material is not always necessary, it always is advantageous to the processing and the end product, to utilize such a material. All percentages recited herein are volume percentages unless otherwise indicated.

The following material densities were used to calculate weight percentages from volume percentages:

Si ₃ N ₄	3.20 Mg/m ³
AlN	3.26
MoSi ₂	6.26
SiC	3.20

Theoretical densities were determined from the material densities assuming the law of mixtures.

For a successful fuel igniter for gas stoves, for example, so-called cold ends are absolutely necessary. Terminal ends or cold ends are made cold by making them much more conductive than the hot-zone. This can be done, for example, by impregnating the terminal ends with metal, or, by varying the composition of a monolithic ceramic resistor from the hot zone out to the terminal ends, with a gradually changing ceramic composition starting with a high resistivity formulation in the hot-zone of the resistor working out to a highly conductive composition in the terminal ends. The present invention favors the latter approach. To accomplish

that end the present igniters preferably have cold ends (terminal ends) made up of 40% to 60% of a nitride, 5% to 30% of silicon carbide and 30% to 50% of molybdenum disilicide and a hot-zone made up of 40% to 60% of a nitride, 10% to 40% of silicon carbide and 5% to 20% of molybdenum disilicide. The compositional transition from the hot-zone into the cold ends may be an abrupt one or a gradual one. When using some compositions of the present invention, a gradual compositional transition is desirable to avoid problems caused by differences in coefficients of thermal expansion of the two zones. On the other hand some compositions are so similar in coefficients of thermal expansion that an abrupt compositional change can be used. Another method for creating cold ends is to design the igniter such that the volume of the terminal ends is at least 5 times greater than the volume of the hot-zone and preferably 5 to 10 times greater.

The preferred nitride is aluminum nitride. To acquire the optimum density and electrical properties the particle sizing of the powders, including the silicon carbide, molybdenum disilicide and sintering aid is not critical except that the particle sizes should be fine enough to allow the resistor itself or the billet from which a heating element or igniter is to be machined, to be pressed to near theoretical density. A suitable particle sizing for

igniter may be designed as a hairpin with a hot zone leg length of 1.0 cm, a leg width of 0.15 cm and a thickness of 0.063 cm. This igniter would operate at 24 volts and 24 watts. A resistivity of 0.09 ohm cm would be achieved by a mixture of 60 volume % AlN, 15.4 volume % MoSi₂, and 24.6 volume % SiC.

An extremely important feature of the electrical device of the invention, particularly in the form of an igniter for fluid fuels, is that because of close control over the resistivity, igniters can be designed to have strong, practical shapes and avoid the large blocky shapes or wire thin configurations which would be necessary using the compositions of the prior art. The practical hot zone of an igniter according to the invention may be defined as follows:

- (1) Thickness or width with a minimum of 0.020 in or a minimum cross-sectional area of 0.0004 in².
- (2) Thickness or width with a maximum of 0.050 or a maximum cross-sectional area of 0.0025 in².
- (3) For thin cross-sections, a hot zone length of a maximum of about 1 in with a ratio of length:area no greater than about 2500 @ 0.004 in².
- (4) For stubby shapes, a hot zone length of at least 0.2 inch as a practical limit.

Such igniters would have the following characteristics:

Size	Area	Ratio	Volts	Resistivity	Watts	Temp.
.2" x .050" x .050"	.0025 in ²	80	110	.346	12.1	1350
.2" x .050" x .050"	.0025 in ²	80	12	.412	12.1	1350
1.0 x .020" x .020"	.0004 in ²	2500	110	.589	21.0	1350
1.0 x .020" x .020"	.0004 in ²	2500	12	.007	21.0	1350

the materials involved is an average particle size of 3 to 5 microns and finer for all materials.

The electrical resistor of the invention can be any one of variety of configurations, depending on its intended end use. It may be very simple in shape such as a straight rod shape with the cold ends or terminal connecting ends on the opposite ends of the body such as that of U.S. Pat. No. 3,252,827. On the other hand the shape could be more complex such as those shown in U.S. Pat. Nos. 3,875,477 and 3,875,476 and Canadian Patent 1,058,673. For use in a gas range for example, a small 1½ inch (4 cm) long ¼ inch (½ cm) wide and 0.4 inch (0.1 cm) thick igniter in a horseshoe or hairpin shape would be most suitable because of stringent space restrictions. However, other configurations may be more desirable in other applications as for example in a clothes drier where the igniter may have to withstand occasional high mechanical forces in which case any igniter shape such as that taught by U.S. Pat. No. 3,875,477.

Because electrical resistivity may be varied over several orders of magnitude, configurations may be designed to accommodate the application rather than the electrical characteristics of the material as is frequently found with silicon carbide igniters. For example, high voltage, low power systems could be designed with reasonable, easily machinable dimensions instead of thin very long rods or coiled wire. A 50 watt igniter operating at 220 volts could be a hairpin with a hot zone 2.1 cm long for each leg with leg width of 0.16 cm and thickness of 0.06 cm. This igniter would require a resistivity of 2.2 ohm cm which would be achieved by a mixture of 50 volume % AlN, 7.8 volume % MoSi₂ and 42.2 volume % SiC. Similarly a low voltage, low power

The present electrical device can be further improved by providing a protective coating thereon. If a resistor of the invention is heated at 1300° C. for 6 hours in air, a protective coating of what is believed to be a mixed oxide is formed on the surface. This coating prevents oxidation of the main body of the resistor particularly the molybdenum disilicide which can undergo oxidation at 400°-500° C. which can result in an undesirable volume change. Another approach is coating an igniter for example with very fine silicon carbide followed by oxidation of the coating to silica. Still a third means of enhancing the life of a resistor is to coat it with either silicon nitride or silicon oxynitride providing such coating is impervious to air.

A very critical property of an igniter, especially if gas is the fuel, is the heat up time i.e. the time for the hot-zone of the igniter to get from room temperature to the ignition temperature of the gas. This is controlled primarily by the ratio of room temperature resistivity to resistivity at 1200° C.; the higher that ratio the longer the heat up time. U.S. Pat. No. 4,205,363 boasts of ratios less than 12, preferably 9 and contains an example where said ratio was as low as 5.5. The same ratio for igniters of the present invention can easily be designed to be less than 5 and as low as 0.2 thus providing igniters with very rapid response or heat up times. Similarly, because igniters are small, mechanical strength becomes important. The composition of the present invention results in an igniter with a modulus of rupture at room temperature using 2 inch (5.08 cm) span with 3 point loading of about 66,000 psi (450 MPa) when the mixture of nitride, carbide and silicide is hot pressed to 99.7% of theoretical density.

Probably the single most important feature of the invention igniter is an unusually low power load per unit area of radiating surface. Igniters made according to the invention consume only about 20 to about 60 watts per square centimeter of radiating surface at 1200° C. To radiate at 1200° C. the hot zone of the igniter requires a load of 34.5 watts/cm² as shown in Example I below and 24.1 watts/cm² as shown in Example II below. Igniters made according to U.S. Pat. No. 4,205,363 require a load of 60 to 100 watts per centimeter. More specifically, the device of Example 2, of that patent requires 82.6 watts/cm² to operate at a similar temperature; Example 3 requires 63.6 watts/cm². The lower load value for the invention igniter means that such an igniter can operate at the desired temperature with 2 to 3 times the radiating surface. This in turn allows igniters to be used that are larger in size and consequently stronger than the fragile prior art igniters such as the essentially hair like igniter of U.S. Pat. No. 4,205,363.

The commercial success of a ceramic igniter is dependent on that device's ability to survive for long periods of time in a very hostile environment without being physically destroyed. A gas igniter for a gas range, for example, should be able to withstand numerous heat-up and cool-down cycles; it should also be able to survive many hours exposure to elevated temperatures and the chemical environment of a gas flame. The present igniters can easily undergo 120,000 cycles and prolonged exposure to a gas flame for over 4000 hours without significant physical damage. However, resisting physical damage is only part of the survival characteristics required in a successful igniter. The other part is the ability of the igniter to go through the foregoing severe and prolonged exposure without a drastic change in the ratio of room temperature resistivity to resistivity of 1200° C., for the reason stated above. Because the resistors of the invention are so stable to deterioration the ratio remains relatively constant.

BRIEF DESCRIPTION OF THE DRAWING

FIGS. 1 and 2 are scanning electron microscope (SEM) photomicrographs of two different compositions of the invention, taken at 2000X.

FIG. 3 is a scanning electron microscope (SEM) photomicrograph of the composition of FIG. 2 taken at 17000X.

FIG. 4 graphically shows the relationship between the slope of the resistivity curve and the ratio of MoS₂:SiC.

FIG. 5 graphically shows the relationship of the ratio of hot resistivity to cold resistivity as a function of MoS₂:SiC.

EXAMPLES OF THE PREFERRED EMBODIMENTS

Example I

Two igniters were fabricated and compared in use. One was a silicon carbide-silicon nitride igniter made according to the Richerson patent U.S. Pat. No. 3,890,250 and the other was made according to the present invention.

A mixture of 60% by weight of silicon nitride and 40% by weight of silicon carbide, according to the Richerson patent, was hot pressed into a billet to a density of 3.08 Mg/m³. The mixture was made up of 3 micron silicon nitride containing 2.5% magnesium carbonate and 3 micron silicon carbide containing 0.8% of

aluminum and hot pressed 1775° C. From the billet an igniter was machined with a hot-zone which measured 0.104 cm×0.106 cm×2.46 cm long which had a resistivity at room temperature of 1.60 ohm-cm and at 1200° C. a resistivity of 0.82 ohm-cm. The igniter was life tested at 1200° C. and it was found that after only 311 hours the resistance of the hot-zone at 1200° C. had increased from 182.4 ohms to 274.4 ohms, an increase of 35.6%. The resistance of the cold ends and electrical connections increased from 40.4 ohms to 154.4 ohms or a change of 282%. It was found that by mixing a substantial quantity of molybdenum disilicide with the silicon carbide, and blending with silicon nitride many of the problems with low density, hot-zone degradation, and high resistance of the cold ends, were overcome.

A mixture of 58.5% silicon nitride 30% silicon carbide, 10% molybdenum disilicide, and 1.5% magnesium carbonate was prepared as follows: The silicon nitride was made from 3 micron silicon and was about 95% alpha silicon nitride. This was blended with reagent grade MgCO₃ powder in isopropyl alcohol in a blender. The silicon carbide used was 3 micron material and was ball milled with finer than 200 mesh molybdenum disilicide for 7-8 hours in isopropyl alcohol using tungsten carbide milling balls. The two mixtures were then blended by rolling together in a ball mill for 30 minutes. This was done to insure that the conductive matrix of silicon carbide and molybdenum disilicide was a homogeneous mixture and yet had a coarse structure without a lot of fine bridges when combined with the silicon nitride. A disc measuring 7.62 cm in diameter and 0.79 cm thick was hot pressed using 155 g of the above mixture dried. The pressing was done in a graphite mold at 1775° C. and a load of 8 Mg with a soak at 1775° C. of approximately one hour. The density of the pressed mixture was 3.356 Mg/m³ with theoretical density being 3.366 Mg/m³; the pressed piece was 99.7% of theoretical. An igniter was machined from this billet or disc. It had a hot-zone measuring 3.18 cm×0.12 cm×0.06 cm with a tab on each end measuring 1.91 cm×0.7 cm×0.06 cm. The ratio of cross section of the cold ends to the cross section of the hot zone was about 11 to 1. The igniter was placed in a furnace and heated at 1300° C. in air for 6 hours. This produced a thin oxide protective coating on the igniter.

Electrical contacts were made on the tabs by first machining 0.25 cm wide by 0.63 cm in from the ends. The igniter was then masked so that only the slotted ends were exposed and the protective oxide film was sand blasted off the exposed ends. A machine screw 2-56× $\frac{1}{2}$ " and 4 Belleville washers and a nut were assembled and tightened in the slot on each end. The four washers flattened with a load of 40 kg; a section of 0.3 mm nickel wire was looped around the screw and held in place with a second nut; the wire was connected electrically. Resistivity at room temperature was 0.252 ohm-cm and dropped to a minimum of 0.146" at 1100° C. then increased to 0.148 ohm-cm at 1300° C. The ratio of resistivities at room temperature to 1200° C. was 1.7.

A life test was run at 1200° C. in air comparing the igniter according to the Richerson patent (Prior Art) and the above invention igniter with the following results:

	Prior Art	Invention
Size of hot zone:		

-continued

	Prior Art	Invention
Width \times thick (cm ²)	.104 \times .106	.109 \times .064
length (cm)	2.46	3.18
Total voltage at start	86.0	56.8
Total amperage at start	.386	.754
Total power at start (watts)	33.2	42.8
Power for hot zone (watts) P_H	27.1	38.0
Hot zone resistance start, R_H	182.4	66.8
Hours of operation	311	908
Hot zone resistance at end, R_H	247.4	70.5
% R_H	35.6	5.5
% R_H/hr	0.114	0.006

These data show that the aging of the invention igniter is considerably less than that of the Prior Art igniter. The resistance change for the invention igniter took place essentially during the first 30 hours when the total change was only 7%. There was essentially no change for an additional 500 hours after which the resistance slowly decreased by about 5.5% based on the original resistance after 908 hours. The igniter actually became more conductive with time at 1200° C. The voltage remained stable after a slight initial increase from 56.2 to 57.0 volts; this was due to a small increase in the resistance of the cold ends. The cold ends operated at a temperature of 260° C. and were stable after the initial 125 hours with essentially no further change taking place. The resistance of the cold ends of the invention igniter decreased from 8.5 ohms to 5.8 ohms after the first 56 hours, showed an increase to 6.6 ohms after 160 hours remaining steady for 600 hours, after which the resistance gradually increased to 7.5 ohms at the 908th hour. The invention igniter changed a total of 29% while the Prior Art igniter changed resistance by 282%. Furthermore, the cold ends or tabs of the Prior Art device were running at 394° C. and 456° C. while the invention igniters cold ends remained at 280° C. and 250° C.

Example II

A double-legged dual composition hairpin or U-shaped igniter made up of aluminum nitride, silicon carbide and molybdenum disilicide was fabricated in the following manner:

Two batches of 101.8 grams and 90.4 grams of through 325 mesh aluminum nitride were ball milled in isopropyl alcohol for 1 hour using a tungsten carbide lined mill and tungsten carbide milling media. Two mixtures of 98.2 grams and 139.6 grams of molybdenum disilicide and silicon carbide were prepared in the same way; the first of these mixtures was made up of 75% molybdenum disilicide and 25% silicon carbide, and the other mixture was 50% molybdenum disilicide and 50% silicon carbide, all percentages being by volume. Two mixtures containing all three materials were prepared to give one with 50-30-20 and the other 60-20-20 volume percent aluminum nitride, molybdenum disilicide and silicon carbide respectively. 40 grams of the high silicon carbide mixture and 47.2 grams of the high molybdenum disilicide mixture in the form of alcohol slips were placed side-by-side in a graphite mold in the form of slips with a graphite spacer between the two; the mold had a cavity measuring 2" \times 2.5" (5.08 cm \times 6.35 cm). The alcohol was removed, and the materials were hot pressed, after completing the assembly of the mold at about 1.2 tons/in² (16.6 MPa) and 1760°-1820° C. in an argon atmosphere to maximum contraction followed by a 60 minute hold. A double-legged hairpin or U-shaped igniter was machined from the billet with the high sili-

con carbide mix making up the hot zone and the high molybdenum disilicide material being in the legs or terminal connecting ends. The hot-zone measured 1.4 cm \times 0.242 cm \times 0.061 cm. The igniter was given a protective glaze or coating by firing it in air at 1350° C. for about 6 hours. The device was electrically connected with alligator clips and caused to heat up to 1200° C.; it was allowed to maintain this temperature for a total lift test of 1988 hours. The resistivity at room temperature was 0.0073 ohm-cm and 0.019 ohm-cm at 1200° C.; at the start the voltage was 13.71, power at 1200° C. was 16.6 watts and the load at 1200° C. was 24.1 watts/cm². The terminals were stable and remained at a relatively constant temperature of 120° C. for 1988 hours. During the life test the total change in resistance was 0.06% of which the hot zone gained 1.64% and the terminal connection lost 1.70%.

What is claimed is:

1. An igniter for fluid fuels comprised of a hot zone and cold ends consisting essentially of a sintered mixture of 5 to 50% by volume of a molybdenum disilicide and 50 to 95% by volume of a mixture of silicon carbide and aluminum nitride; 4% or less of open porosity, a room temperature flexural strength of at least 30,000 psi (207 MPa), a resistivity range of from 0.0001 to 90 ohm centimeters, a ratio of room temperature resistivity to that at 1200° C. of from 0.2 to 19.8, a response time from room temperature to about 1200° C. of less than 25 seconds, said igniter consuming from about 20 to about 50 watts per square centimeter of radiating surface at 1200° C.

2. The igniter of claim 1 wherein said igniter consists essentially of 30% to 70% by volume of aluminum nitride, 5% to 40% by volume of silicon carbide, 5% to 50% by volume of molybdenum disilicide, and 0 to 3% by weight of a sintering aid.

3. The igniter of claim 1 wherein the composition varies from the hot zone to the cold ends such that said cold ends are made up of all molybdenum disilicide.

4. The igniter of claim 3 wherein the composition changes gradually from hot zone to cold ends.

5. The igniter of claim 3 wherein the composition varies abruptly from hot zone to cold ends.

6. The igniter of claim 2 having cold ends and a hot zone with a resistivity differential therebetween which is the result of said cold ends being made up of 30% to 70% by volume of said nitride, 5% to 30% by volume of silicon carbide, and 30% to 50% by volume of molybdenum disilicide; and said hot-zone is made up of 30% to 70% by volume of said nitride, 10% to 40% by volume of silicon carbide, and 5% to 20% by volume of molybdenum disilicide.

7. The igniter of claim 2 wherein said igniter is formed from 40% to 65% by volume of aluminum nitride powder having an average particle size of about 3 microns, 10% to 40% by volume of silicon carbide having an average particle size of about 3 microns, 5% to 50% by volume of molybdenum disilicide having a particle size of about 3 microns, and wherein said resistor has a density of at least 2.80 Mg/m³.

8. The igniter of claim 1 having cold ends and a hot zone wherein the resistance differential between the cold ends and the hot zone is a result of the cold ends having a volume 5 to 10 times greater than the volume of the hot zone.

9. The igniter of claim 1 which is provided with a protective mixed oxide coating.

10. The igniter of claim 1 which includes a protective coating thereon selected from the group consisting of silica, silicon oxynitride and silicon nitride.

* * * * *

RELATED PROCEEDINGS APPENDIX D

No decisions have been identified above pursuant to 37 CFR 41.37(c)(1)(ii).